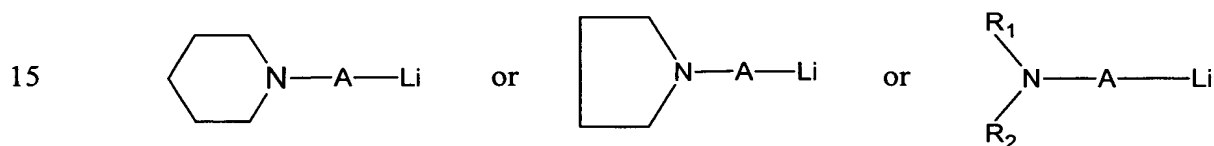# FUNCTIONALIZED MONOMERS FOR SYNTHESIS OF RUBBERY POLYMERS

Background of the Invention

It is important for rubbery polymers that are used in tires, hoses, power transmission belts and other industrial products to have good compatibility with fillers, such as carbon black and silica. To attain improved interaction with fillers such rubbery polymers can be functionalized with various compounds, such as amines. United States Patent 4,935,471 discloses a process for preparing a polydiene having a high level of affinity for carbon black which comprises reacting a metal terminated polydiene with a capping agent selected from the group consisting of (a) halogenated nitriles having the structural formula X-A-C≡N, wherein X represents a halogen atom and wherein A represents an alkylene group containing from 1 to 20 carbon atoms, (b) heterocyclic aromatic nitrogen containing compounds, and (c) alkyl benzoates. The capping agents disclosed by United States Patent 4,935,471 react with metal terminated polydienes and replace the metal with a terminal cyanide group, a heterocyclic aromatic nitrogen containing group or a terminal group which is derived from an alkyl benzoate. For example, if the metal terminated polydiene is capped with a nitrile, it will result in the polydiene chains being terminated with cyanide groups. The use of heterocyclic aromatic nitrogen containing compounds as capping agents can result in the polydiene chains being terminated with a pyrrolyl group, an imidazolyl group, a pyrazolyl group, a pyridyl group, a pyrazinyl group, a pyrimidinyl group, a pyridazinyl group, an indolizinyl group, an isoindolyl group, a 3-H-indolyl group, a cinnolinyl group, a pyridinyl group, a .beta.-carbolinyl group, a perimidinyl group, a phenanthrolinyl group or the

like.

    United States Patent 4,935,471 also discloses that lithium amides are highly preferred initiators because they can be used to prepare polydienes which are terminated with
polar groups at both ends of their polymer chains. The extra polar functionality provided by lithium amides results in increased interaction with carbon black resulting in better polymer-carbon black dispersion. The lithium amides disclosed by United States Patent 4,935,471 include lithium pyrrolidide. United States Patent 4,935,471 also indicates that preferred initiators include amino alkyl lithium compounds of the structural formula:
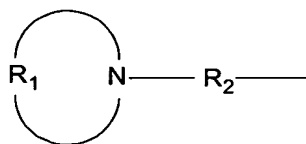
$$
\left\langle \bigcirc \right\rangle\!N\!-\!A\!-\!Li \quad or \quad \left[\:\right\rangle\!N\!-\!A\!-\!Li \quad or \quad \begin{array}{c} R_1 \\ \diagdown \\ N\!-\!A\!-\!Li \\ \diagup \\ R_2 \end{array}
$$

wherein A represents an alkylene group containing from 1 to 20 carbon atoms, and wherein R_1 and R_2 can be the same or different and represent alkyl groups containing from 1 to 20 carbon atoms.

    It is also desirable for synthetic rubbers to exhibit low levels of hysteresis. This is particularly important in the case of rubbers that are used in tire tread compounds. Such polymers are normally compounded with sulfur, carbon black, accelerators, antidegradants and other desired rubber chemicals and are then subsequently vulcanized or cured into the form of a useful article. It has been established that the physical properties of such cured rubbers depend upon the degree to which the carbon black is homogeneously dispersed throughout the polydiene rubber. This is in turn related to the level of affinity that carbon black has for the rubber. This can be of

practical importance in improving the physical
characteristics of rubber articles that are made utilizing
polydiene rubbers. For example, the rolling resistance and
tread wear characteristics of tires can be improved by
5   increasing the affinity of carbon black to the rubbery
polymers utilized therein. Therefore, it would be highly
desirable to improve the affinity of a given polydiene
rubber for carbon black and/or silica. This is because a
better dispersion of carbon black throughout polydiene
10 rubbers which are utilized in compounding tire tread
compositions results in a lower hysteresis value and
consequently tires made therefrom have lower rolling
resistance. It is also known that a major source of
hysteresis is due to polymer chain ends that are not
15 capable of full elastic recovery. Accordingly, improving
the affinity of the rubber chain ends to the filler is
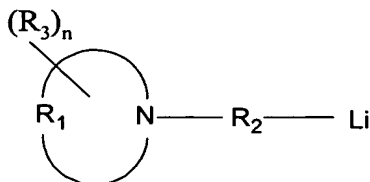extremely important in reducing hysteresis.

United States Patent 6,080,835 discloses a
functionalized elastomer comprising: a functional group
20 defined by the formula:

$$R_1 \quad N \text{———} R_2 \text{———}$$

25 where R_1 is a selected from the group consisting of a
divalent alkylene group, an oxy-alkylene group, an amino
alkylene group, and a substituted alkylene group, each
group having from about 6 to about 20 carbon atoms, R_2 is
covalently bonded to the elastomer and is selected from the
30 group consisting of a linear-alkylene group, a branched-
alkylene group, and a cyclo-alkylene group, each group
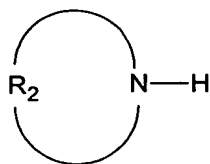having from about 2 to about 20 carbon atoms.

United States Patent 5,932,662 discloses a method of

preparing a polymer comprising: preparing a solution of one or more anionically polymerizable monomers in a solvent; and, polymerizing under effective conditions, said monomers in the presence of a polymerization initiator having the

5   formula

$$R_1 \underset{\displaystyle (R_3)_n}{\diagup} N {-} R_2 {-} Li$$

10

wherein R_1 is a divalent alkylene, an oxy- or amino-alkylene having from 6 to about 20 carbon atoms; and, R_2 is a linear-alkylene, branched-alkylene, or cyclo-alkylene having from about 2 to about 20 carbon atoms, Li is a lithium atom

15   bonded directly to a carbon atom of R_2; and R_3 is a tertiary amino, an alkyl having from about 1 to about 12 carbon atoms; an aryl having from about 6 to about 20 carbon atoms; an alkaryl having from about 7 to about 20 carbon atoms; an alkenyl having from about 2 to about 12 carbon

20   atoms; a cycloalkyl having from about 5 to about 20 carbon atoms; a cycloalkenyl having from about 5 to about 20 carbon atoms; a bicycloalkyl having from about 6 to about 20 carbon atoms; and, a bicycloalkenyl having from about 6 to about 20 carbon atoms; where n is an integer of from 0
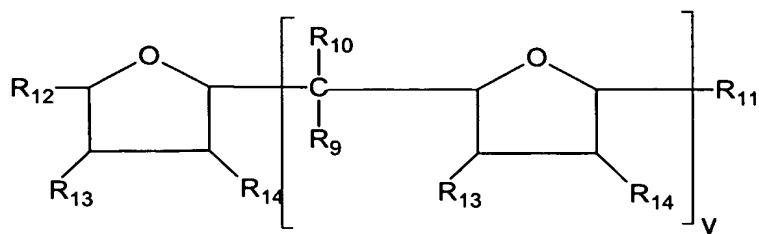
25   to about 10.

United States Patent 6,084,025 discloses a functionalized polymer prepared by a process comprising the steps of: preparing a solution of a cyclic amine compound, an organolithium compound, and from 3 to about 300

30   equivalents, based upon one equivalent of lithium, of a monomer selected from vinyl aromatic monomers, and mixtures thereof, where said cyclic amine compound is defined by the formula

$$R_2 \qquad N—H$$

where R_2 is selected from the group consisting of an alkylene, substituted alkylene, bicycloalkane, and oxy- or N-alkylamino-alkylene group having from about 3 to about 16 methylene groups, N is a nitrogen atom, and H is a hydrogen atom, thereby forming a polymerization initiator having the formula $A(SOL)_yLi$, where Li is a lithium atom, SOL is a divalent hydrocarbon group having from 3 to about 300 polymerized monomeric units, y is from 0.5 to about 3, and A is a cyclic amine radical derived from said cyclic amine; charging the solution containing $A(SOL)_yLi$ with from about 0.01 to about 2 equivalents per equivalent of lithium of a chelating reagent, and an organic alkali metal compound selected from compounds having the formula R_4OM, $R_5C(O)OM$, R_6R_7NM, and R_8SO_3M, where R_4, R_5, R_6, R_7, and R_8 are each selected from alkyls, cycloalkyls, alkenyls, aryls, or phenyls, having from 1 to about 12 carbon atoms; and where M is Na, K, Rb or Cs, and sufficient monomer to form a living polymeric structure; and quenching the living polymeric structure.
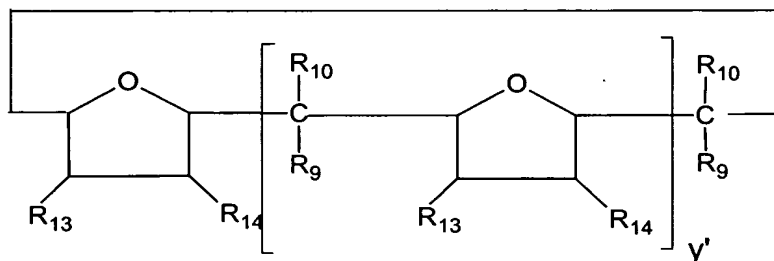
In the initiator systems of United States Patent 6,084,025 a chelating reagent can be employed to help prevent heterogeneous polymerization. The reagents that are reported as being useful include tetramethylethylenediamine (TMEDA), oxolanyl cyclic acetals, and cyclic oligomeric oxolanyl alkanes. The oligomeric oxolanyl alkanes may be represented by the structural formula:

5

and

10

15

wherein R_9 and R_{10} independently are hydrogen or an alkyl group and the total number of carbon atoms in $-CR_9R_{10}-$ranges

20   between one and nine inclusive; y is an integer of 1 to 5 inclusive; y' is an integer of 3 to 5 inclusive; and R_{11}, R_{12}, R_{13}, and R_{14} independently are -H or $-C_nH_{2n+1}$, wherein n=1 to 6.

        United States Patent 6,344,538 discloses
25   functionalized monomers and polymerized functionalized monomers selected from the group consisting of 2-(N,N-dimethylaminomethyl)-1,3-butadiene, 2-(N,N-diethylaminomethyl)-1,3-butadiene, 2-(N,N-di-n-propylaminomethyl)-1,3-butadiene, 2-(cyanomethyl)-1,3-
30   butadiene, 2-(aminomethyl)-1,3-butadiene, 2-(hydroxymethyl)-1,3-butadiene, 2-(carboxymethy)-1,3-butadiene, 2-(acetoxymethyl)-1,3-butadiene, 2-(2-alkoxy-2-oxoethyl)-1,3-butadiene, 2,3-bis(cyanomethyl)-1,3-
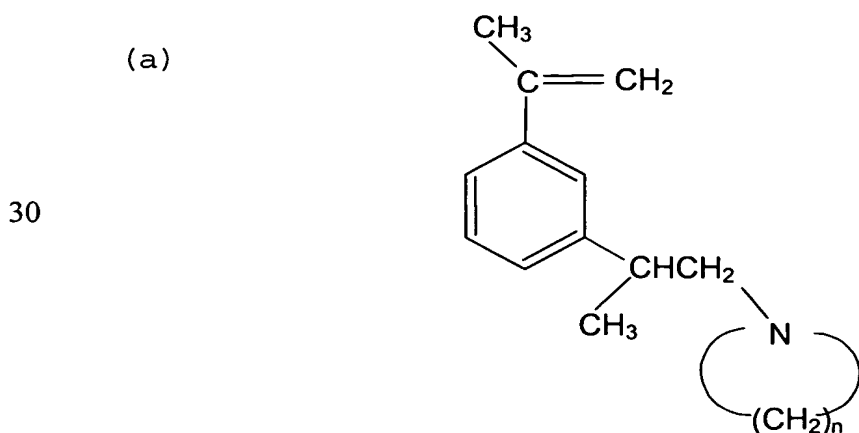
butadiene, 2,3-bis(dialkylaminomethyl)-1,3-butadiene, 2,3-bis(4-ethoxy-4-4-oxobutyl)-1,3-butadiene and 2,3-bis(3-cyanopropyl)-1,3-butadiene, and methods for preparing such functionalized diene monomers and polymers.

5

Summary of the Invention

The present invention relates to functionalized monomers that can be polymerized into rubbery polymers having low hysteresis and good compatibility with fillers,
10 such as carbon black and silica. The functionalized monomers of this invention are typically incorporated into the rubbery polymer by being copolymerized with one or more conjugated diolefin monomers and optionally other monomers that are copolymerizable therewith, such as vinyl aromatic
15 monomers. In any case, improved polymer properties are realized because the functionalized monomers of this invention improve the compatibility of the rubber with the types of fillers that are typically used in rubber compounds, such as carbon black and silica.
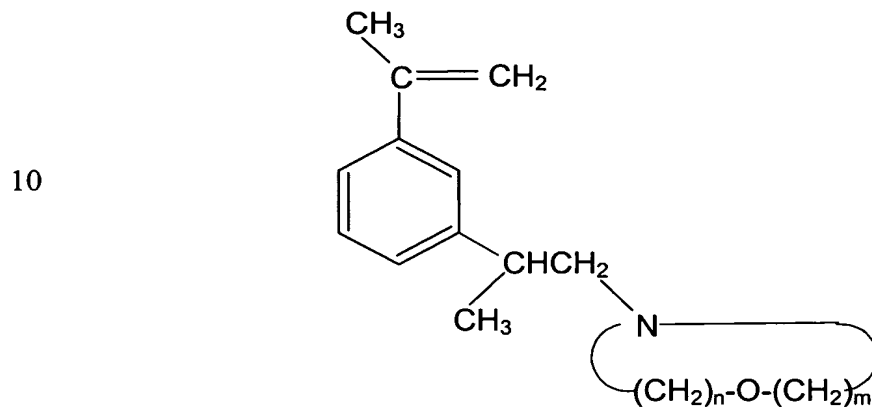
20 This invention more specifically discloses monomers that are particularly useful for copolymerization with conjugated diolefin monomers to produce rubbery polymers having better compatibility with fillers. The monomers of this invention have a structural formula selected from the
25 group consisting of

(a)

wherein n represents an integer from 4 to about 10,

5

(b)

$$CH_3-C=CH_2$$

(structure: 3-substituted phenyl ring bearing a $CH_3-C=CH_2$ isopropenyl group and a $CHCH_2$ with CH_3, connected to N with ring $-(CH_2)_n-O-(CH_2)_m-$)

10

15

wherein n represents an integer from 0 to about 10 and
wherein m represents an integer from 0 to about 10, with
the proviso that the sum of n and m is at least 4;

20   (c)

$$CH_3-C=CH_2$$

(structure: phenyl ring bearing isopropenyl group and $CHCH_2$ with CH_3, connected to N bearing R and R')

25

wherein R and R' can be the same or different and represent
30   alkyl, allyl groups or alkoxy groups containing from about
1 to about 10 carbon atoms;

(d)

wherein n represents an integer from 1 to about 10, and wherein R and R' can be the same or different and represent alkyl groups containing from about 1 to about 10 carbon atoms;

(e)

wherein n represents an integer from 1 to about 10 and wherein m represents an integer from 4 to about 10;

(f)
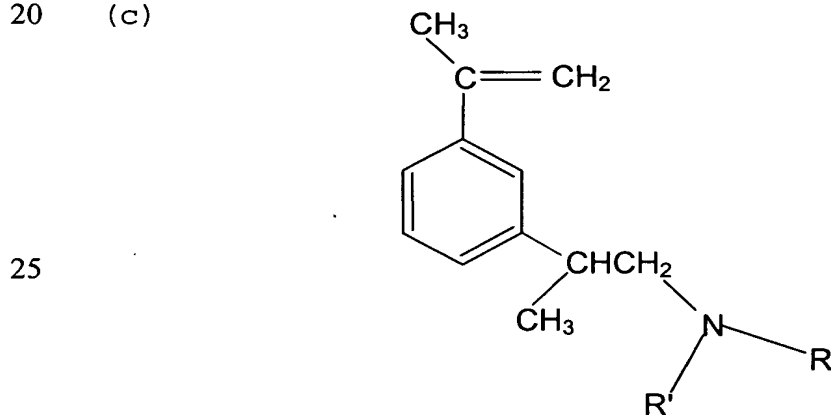

wherein x represents an integer from about 1 to about 10,

wherein n represents an integer from 0 to about 10 and
wherein m represents an integer from 0 to about 10, with
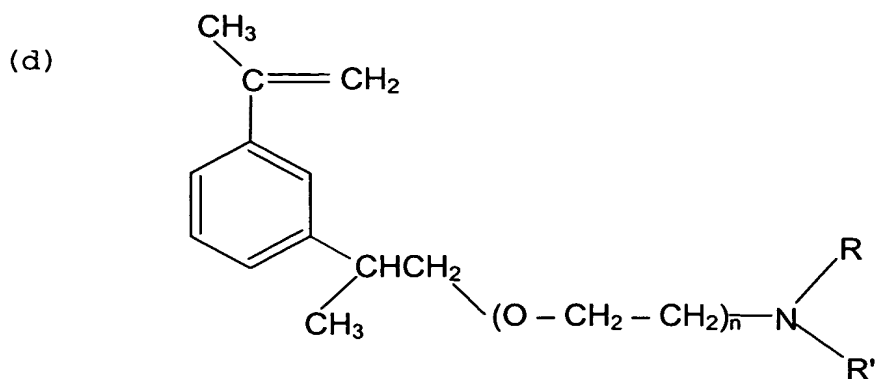the proviso that the sum of n and m is at least 4;

5   (g)

R, R', N, H₂C, CH₂ structure

10

wherein R and R' can be the same or different and represent
allyl, alkoxyl or alkyl groups containing from 1 to about
10 carbon atoms,

15

(h)

N, (CH₂)m, H₂C, CH₂ structure

20

wherein m represents an integer from about 4 to about 10;

25   (i)

CH₃, C=CH₂, CH₃, CHCH₂, N, (CH₂)n-N-(CH₂)m, R structure

30

wherein R represents a hydrogen atom or an alkyl group
containing from 1 to about 10 carbon atoms, wherein n
represents an integer from 0 to about 10, and wherein m
represents an integer from 0 to about 10, with the proviso
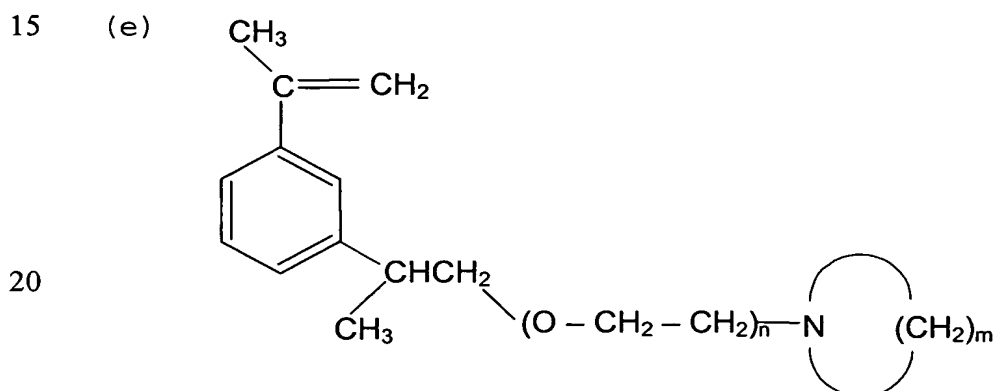that the sum of n and m is at least 4; and

(j)

wherein n represents an integer from 0 to about 10, wherein
m represents an integer from 0 to about 10, wherein x
represents an integer from 1 to about 10, and wherein y
represents an integer from 1 to about 10.

The present invention further discloses a process for
synthesizing an amine functionalized monomer that comprises
(1) reacting a secondary amine with a 2,3-dihalopropene to
produce a vinyl halide containing secondary amine having a
structural formula selected from the group consisting of

(a)

wherein R and R′ can be the same or different and represent
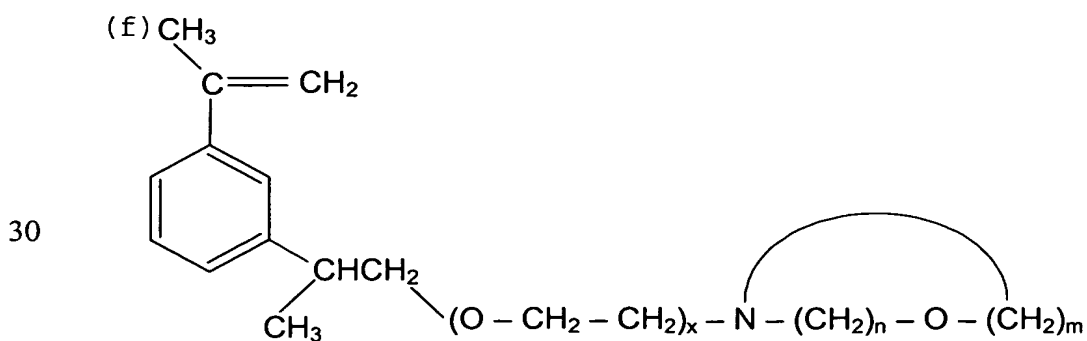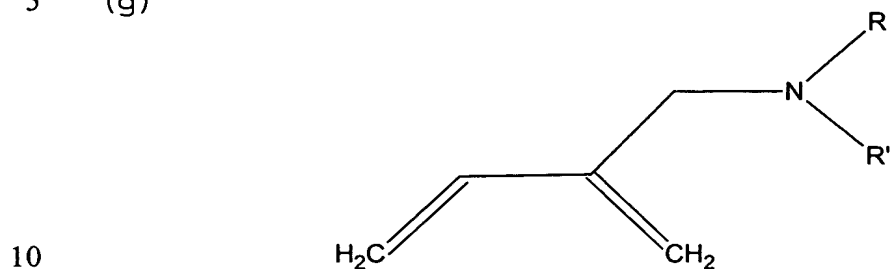allyl, alkoxyl or alkyl groups containing from 1 to about
10 carbon atoms, and wherein X represents a halogen atom,
and

5

(b)

10

wherein m represents an integer from 4 to about 10, and
wherein X represents a halogen atom; and (2) reacting the
vinyl halide containing secondary amine with a vinyl
magnesium halide to produce the monomer, wherein the
15   monomer has a structural formula selected from the group
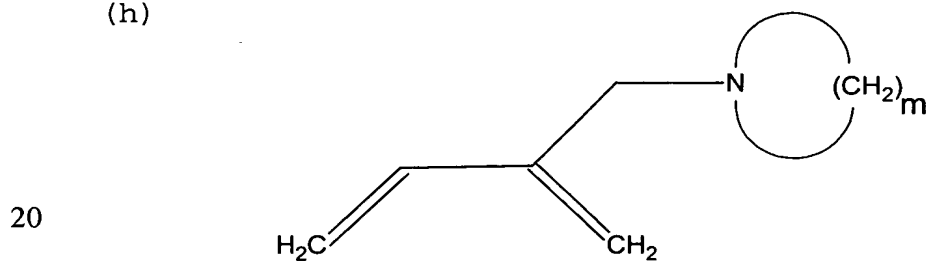consisting of

(a)

20

wherein R and R′ can be the same or different and represent
25   allyl, alkoxyl or alkyl groups containing from 1 to about
10 carbon atoms, and
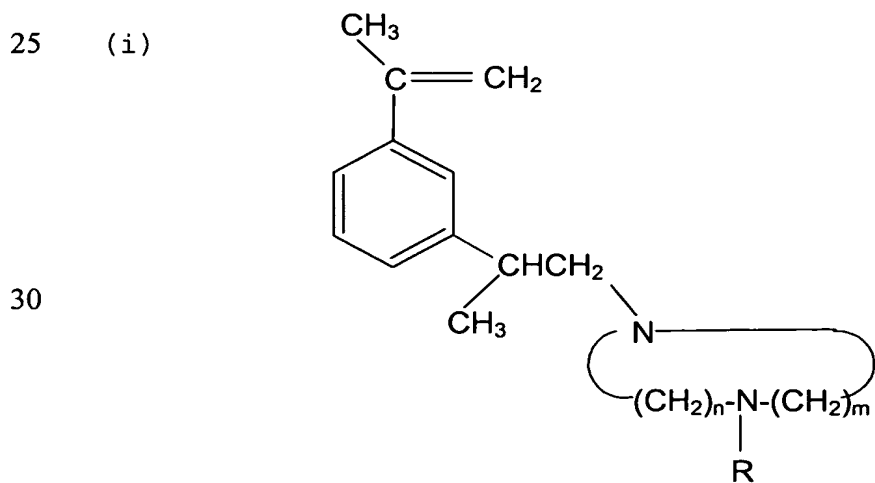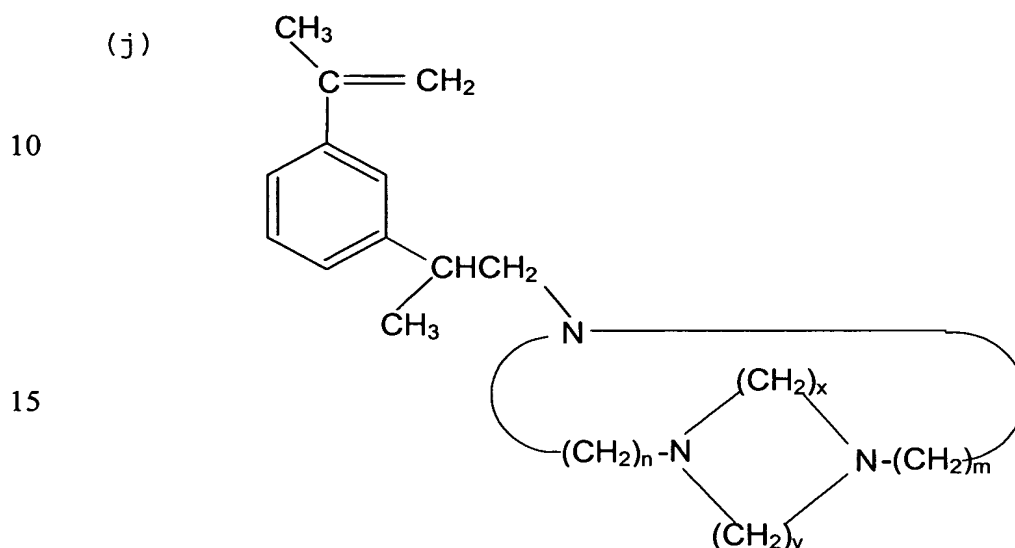
(b)

30

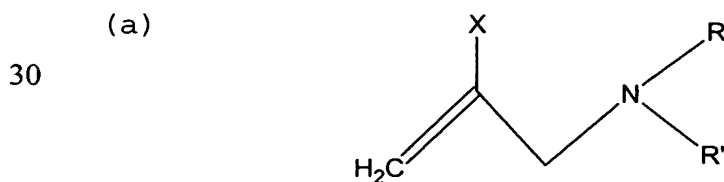wherein m represents an integer from about 4 to about 10.

The present invention also reveals a rubbery polymer which is comprised of repeat units that are derived from (1) at least one conjugated diolefin monomer, and (2) at least one monomer having a structural formula selected from the group consisting of

(a)

$$CH_3$$
$$C = CH_2$$

CHCH$_2$
CH$_3$
N
(CH$_2$)$_n$

wherein n represents an integer from 4 to about 10,

(b)

$$CH_3$$
$$C = CH_2$$

CHCH$_2$
CH$_3$
N
(CH$_2$)$_n$-O-(CH$_2$)$_m$

wherein n represents an integer from 0 to about 10 and wherein m represents an integer from 0 to about 10, with the proviso that the sum of n and m is at least 4;

(c)

$$CH_3$$
$$C = CH_2$$

wherein R and R' can be the same or different and represent alkyl, allyl groups or alkoxy groups containing from about 1 to about 10 carbon atoms;

(d)

$$CH_3$$
$$C = CH_2$$

$$CHCH_2$$
$$CH_3$$
$$(O - CH_2 - CH_2)_n - N \begin{array}{c} R \\ R' \end{array}$$

wherein n represents an integer from 1 to about 10, and wherein R and R' can be the same or different and represent alkyl groups containing from about 1 to about 10 carbon atoms;

(e)

$$CH_3$$
$$C = CH_2$$

$$CHCH_2$$
$$CH_3$$
$$(O - CH_2 - CH_2)_n - N \quad (CH_2)_m$$

wherein n represents an integer from 1 to about 10 and
wherein m represents an integer from 4 to about 10;

(f)

$$CH_3$$
$$C \!=\!\!= CH_2$$

phenyl ring with:

$$CHCH_2$$
$$CH_3 \quad (O - CH_2 - CH_2)_x - N - (CH_2)_n - O - (CH_2)_m$$

wherein x represents an integer from about 1 to about 10,
wherein n represents an integer from 0 to about 10 and
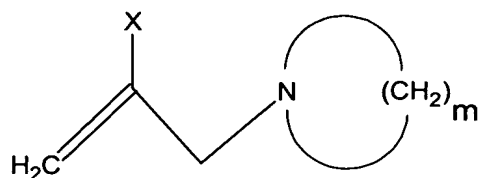wherein m represents an integer from 0 to about 10, with
the proviso that the sum of n and m is at least 4;

(g)

$$R$$
$$N$$
$$R'$$

$$H_2C \qquad CH_2$$

wherein R and R′ can be the same or different and represent
allyl, alkoxyl or alkyl groups containing from 1 to about
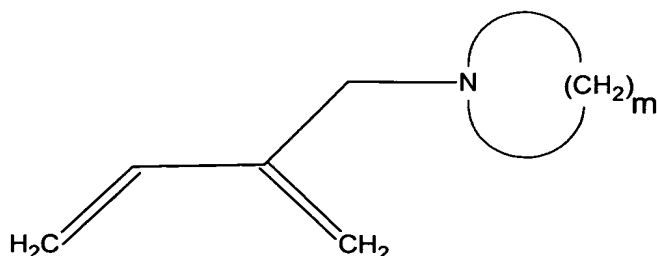10 carbon atoms,

(h)

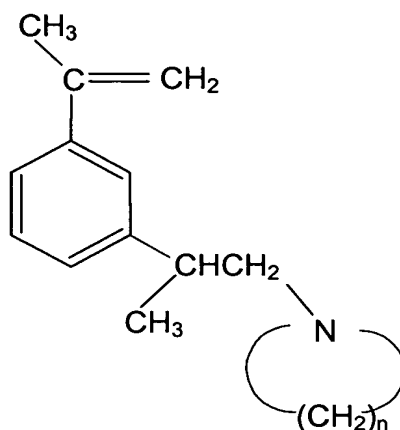$$N \quad (CH_2)_m$$

$$H_2C \qquad CH_2$$

wherein m represents an integer from about 4 to about 10;

(i)

$$CH_3$$
$$C = CH_2$$

$$-(CH_2)_n-N-(CH_2)_m$$
$$R$$

wherein R represents a hydrogen atom or an alkyl group
containing from 1 to about 10 carbon atoms, wherein n
represents an integer from 0 to about 10, and wherein m
represents an integer from 0 to about 10, with the
provision that the sum of n and m is at least 4; and

(j)

$$CH_3$$
$$C = CH_2$$

wherein n represents an integer from 0 to about 10, wherein
m represents an integer from 0 to about 10, wherein x
represents an integer from 1 to about 10, and wherein y
represents an integer from 1 to about 10.

The subject invention further discloses a process for

synthesizing a rubbery polymer that comprises
copolymerizing at least one conjugated diolefin monomer and
at least one functionalized monomer in an organic solvent
at a temperature which is within the range of 20°C to about
5   100°C, wherein the polymerization is initiated with an
anionic initiator, wherein the polymerization is conducted
in the presence of an alkali metal alkoxide, and wherein
the functionalized monomer has a structural formula
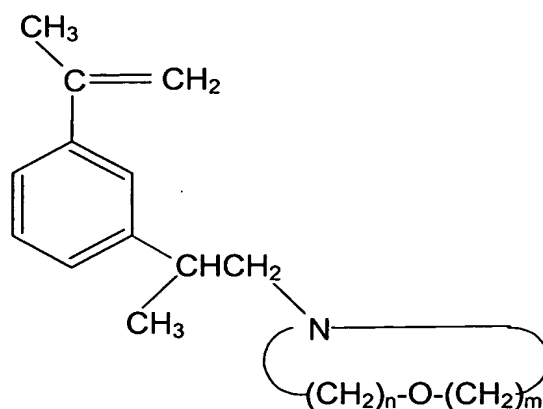selected from the group consisting of

10

(a)

20
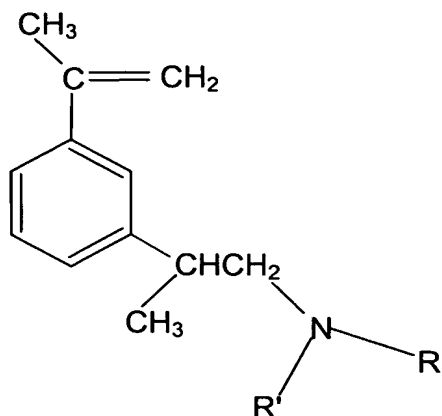
wherein n represents an integer from 4 to about 10,

(b)

wherein n represents an integer from 0 to about 10 and

wherein m represents an integer from 0 to about 10, with the proviso that the sum of n and m is at least 4;
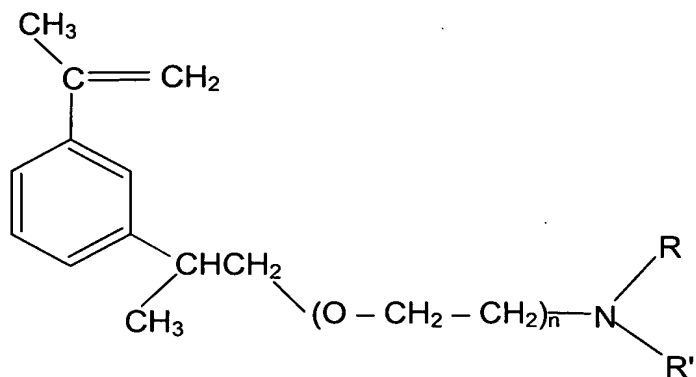
(c)

wherein R and R′ can be the same or different and represent alkyl, allyl groups or alkoxy groups containing from about 1 to about 10 carbon atoms;
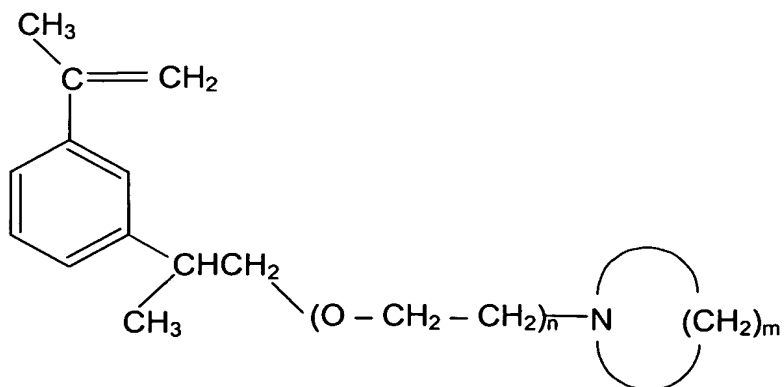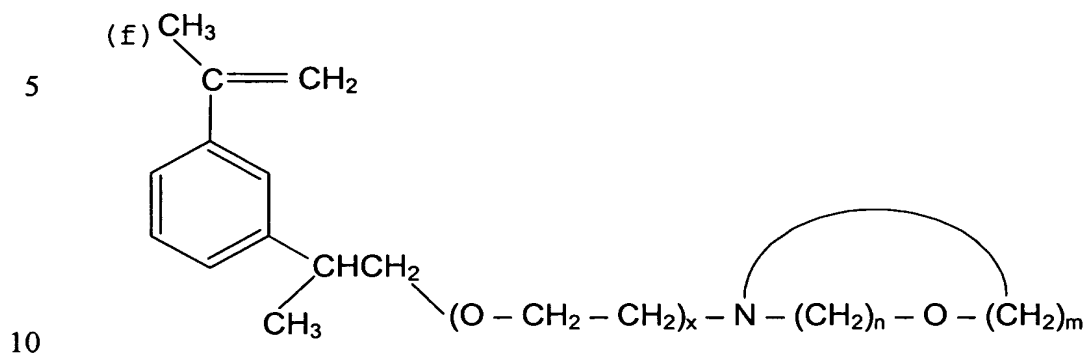
(d)

wherein n represents an integer from 1 to about 10, and wherein R and R′ can be the same or different and represent alkyl groups containing from about 1 to about 10 carbon atoms;

(e)

wherein n represents an integer from 1 to about 10 and
wherein m represents an integer from 4 to about 10;

(f)

wherein x represents an integer from about 1 to about 10,
wherein n represents an integer from 0 to about 10 and
wherein m represents an integer from 0 to about 10, with
the proviso that the sum of n and m is at least 4;

(g)

wherein R and R' can be the same or different and represent
alkyl groups containing from 1 to about 10 carbon atoms,

(h)

wherein m represents an integer from about 4 to about 10;

(i)

wherein R represents a hydrogen atom or an alkyl group
containing from 1 to about 10 carbon atoms, wherein n
represents an integer from 0 to about 10, and wherein m
represents an integer from 0 to about 10, with the proviso
that the sum of n and m is at least 4; and
and

(j)

$$CH_3$$
$$C = CH_2$$

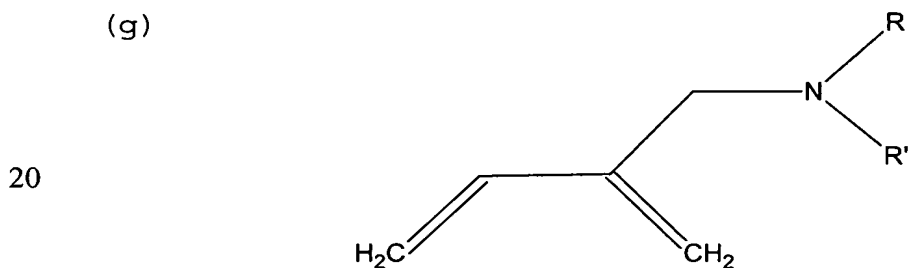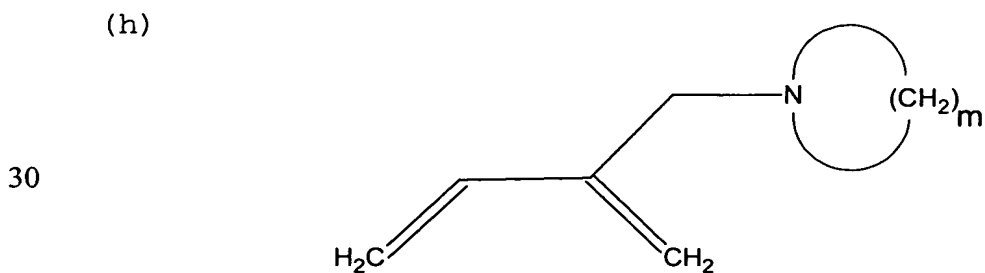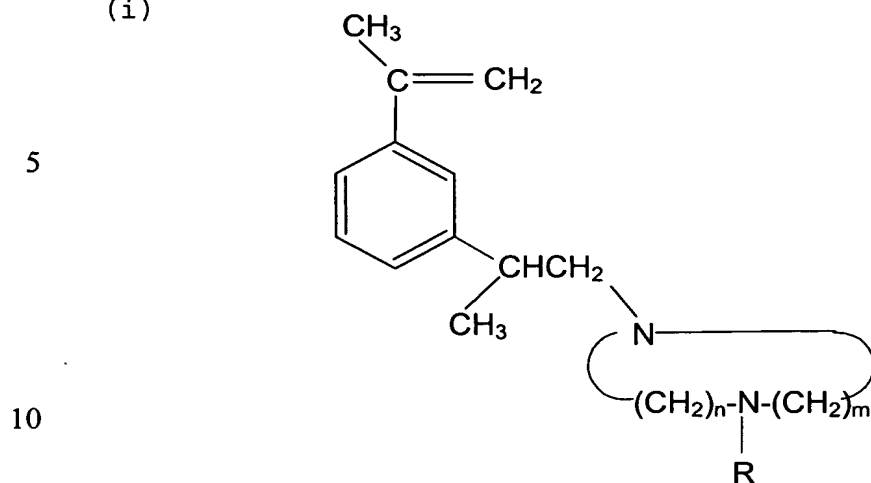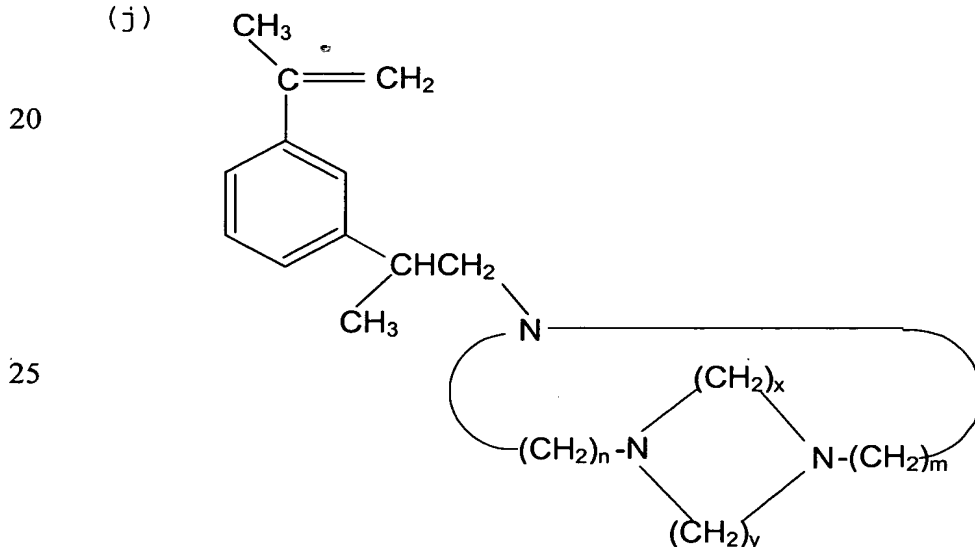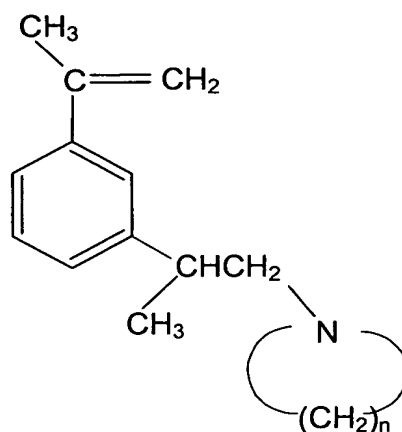(structure with benzene ring, CHCH$_2$, CH$_3$, N, (CH$_2$)$_n$-N, (CH$_2$)$_x$, N-(CH$_2$)$_m$, (CH$_2$)$_v$)

wherein n represents an integer from 0 to about 10, wherein
m represents an integer from 0 to about 10, wherein x
represents an integer from 1 to about 10, and wherein y
represents an integer from 1 to about 10.

The present invention also discloses a process
synthesizing functionalized styrene monomer that comprises
(1) reacting a secondary amine with sodium hydroxide to
produce a sodium amide, and (2) reacting the sodium amide
with a vinyl benzyl halide to produce the functionalized
styrene monomer.

The subject invention further reveals a tire which is
comprised of a generally toroidal-shaped carcass with an
outer circumferential tread, two spaced beads, at least one
ply extending from bead to bead and sidewalls extending
radially from and connecting said tread to said beads,
wherein said tread is adapted to be ground-contacting, and
wherein said tread is comprised of (I) a filler, and (II)
rubbery polymer which is comprised of repeat units that are
derived from (1) at least one conjugated diolefin monomer,
and (2) at least one monomer having a structural formula
selected from the group consisting of

(a)

5

$$\begin{array}{c} CH_3 \\ | \\ C = CH_2 \\ \end{array}$$

[Structure: a benzene ring with a 1-methylethenyl group (CH₃–C=CH₂) at the meta position, and a –CHCH₂–N< group with a CH₃ substituent; the nitrogen is part of a ring closed by –(CH₂)ₙ–]

10

wherein n represents an integer from 4 to about 10,

(b)

15

$$\begin{array}{c} CH_3 \\ | \\ C = CH_2 \\ \end{array}$$

[Structure: a benzene ring with a 1-methylethenyl group (CH₃–C=CH₂) at the meta position, and a –CHCH₂–N< group with a CH₃ substituent; the nitrogen is part of a ring closed by –(CH₂)ₙ–O–(CH₂)ₘ–]

20

wherein n represents an integer from 0 to about 10 and
wherein m represents an integer from 0 to about 10, with

25   the proviso that the sum of n and m is at least 4;

(c)

$$CH_3 - C = CH_2$$

(structure c: a benzene ring with an isopropenyl group $CH_3-C=CH_2$ at one position and a $-CHCH_2-$ group bearing CH_3 connected to N with substituents R and R')

wherein R and R' can be the same or different and represent allyl groups or alkoxy groups containing from about 1 to about 10 carbon atoms;

(d)

$$CH_3 - C = CH_2$$

(structure d: a benzene ring with an isopropenyl group $CH_3-C=CH_2$ and a $-CHCH_2-$ group bearing CH_3 connected through $(O-CH_2-CH_2)_{\overline{n}}-N$ with substituents R and R')

wherein n represents an integer from 1 to about 10, and wherein R and R' can be the same or different and represent alkyl groups containing from about 1 to about 10 carbon atoms;

(e)

$$CH_3 - C = CH_2$$

(structure e: a benzene ring with an isopropenyl group $CH_3-C=CH_2$ and a $-CHCH_2-$ group bearing CH_3 connected through $(O-CH_2-CH_2)_{\overline{n}}-N$ with a ring $(CH_2)_m$)

wherein n represents an integer from 1 to about 10 and
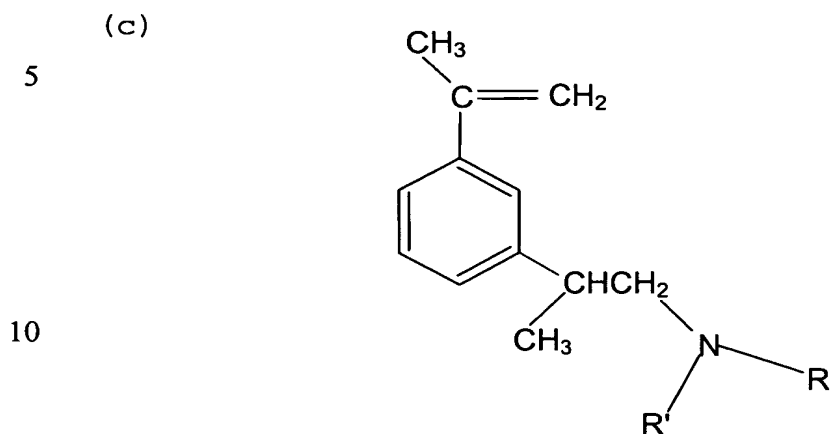wherein m represents an integer from 4 to about 10;

(f)

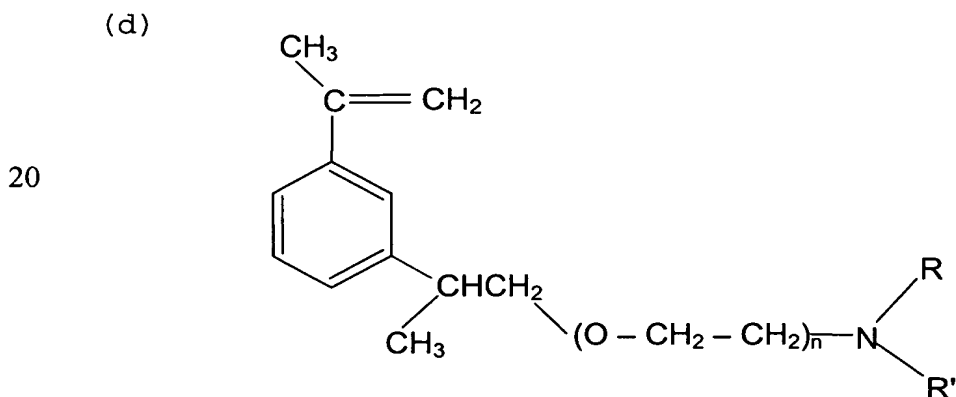wherein x represents an integer from about 1 to about 10,
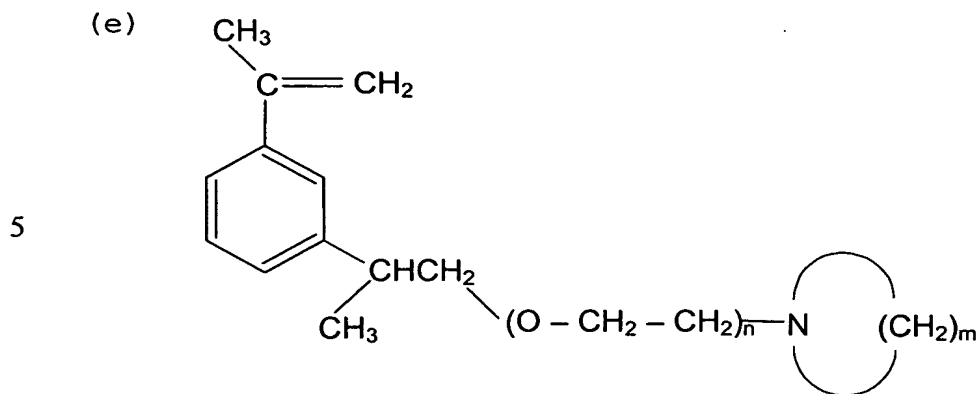wherein n represents an integer from 0 to about 10 and
wherein m represents an integer from 0 to about 10, with
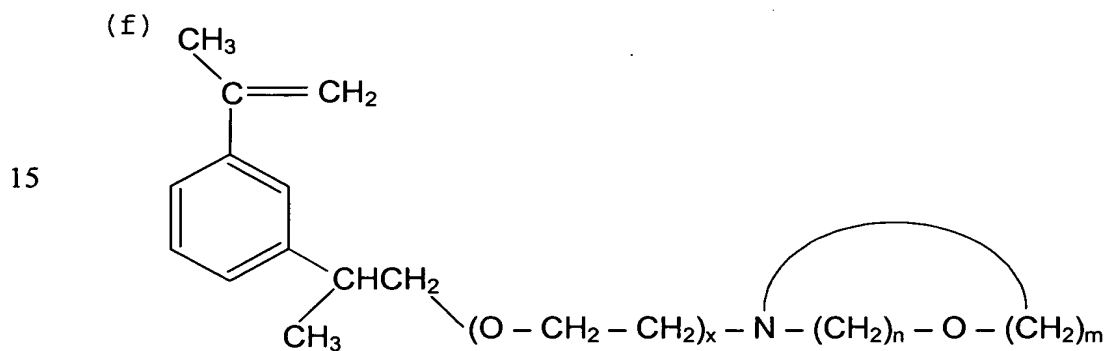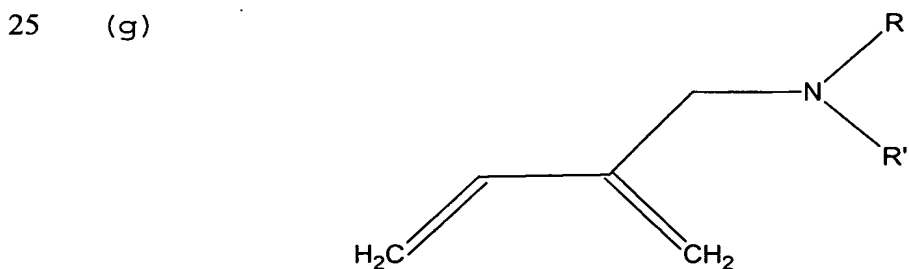the proviso that the sum of n and m is at least 4;

(g)

wherein R and R' can be the same or different and represent
alkyl groups containing from 1 to about 10 carbon atoms,

(h)

wherein m represents an integer from about 4 to about 10;

(i)

$$
\begin{array}{c}
CH_3 \\
| \\
C = CH_2 \\
\end{array}
$$

[structure showing a benzene ring with an isopropenyl group (CH₃-C=CH₂) at one position and a -CHCH₂- group with CH₃ substituent connecting to a cyclic amine at another position; the ring contains N and -(CH₂)ₙ-N-(CH₂)ₘ- with R on the lower nitrogen]

wherein R represents a hydrogen atom or an alkyl group containing from 1 to about 10 carbon atoms, wherein n represents an integer from 0 to about 10, and wherein m represents an integer from 0 to about 10, with the proviso that the sum of n and m is at least 4; and
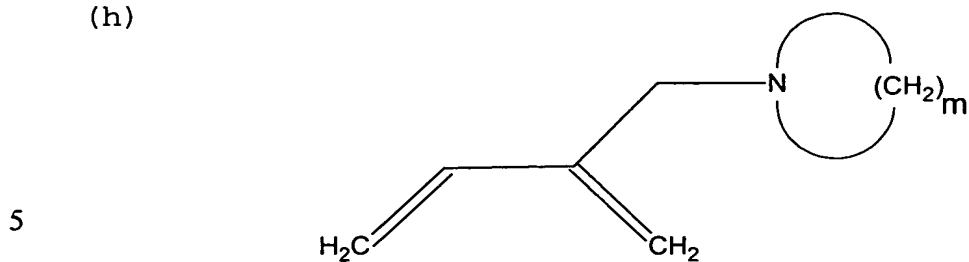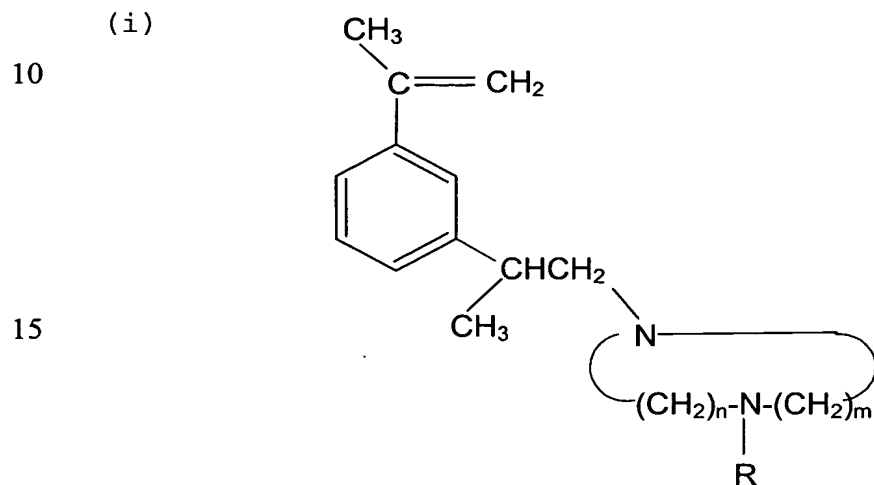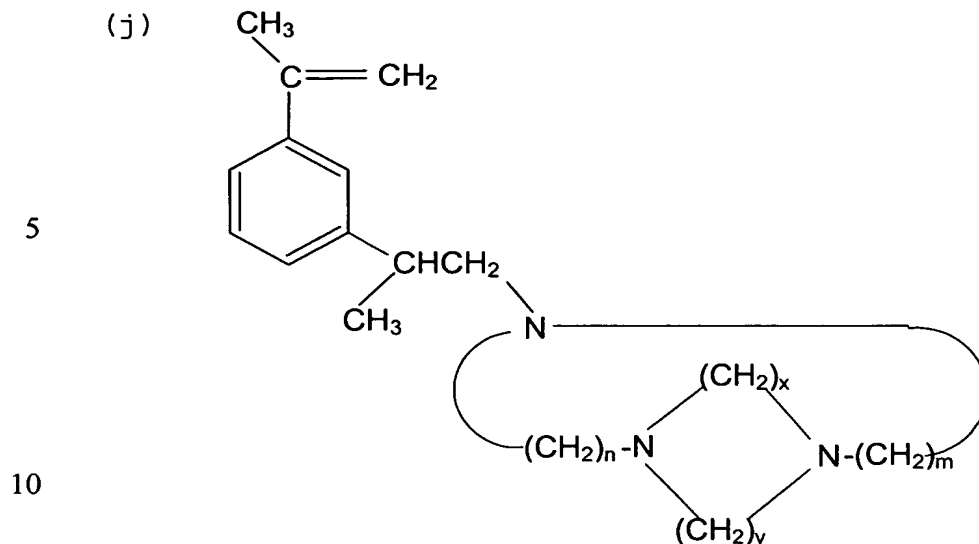and

(j)

$$
\begin{array}{c}
CH_3 \\
| \\
C = CH_2 \\
\end{array}
$$

[structure showing a benzene ring with an isopropenyl group (CH₃-C=CH₂) and a -CHCH₂- group with CH₃ substituent connecting to a bicyclic amine system with N, -(CH₂)ₙ-N-, -(CH₂)ₓ, (CH₂)ᵧ, and N-(CH₂)ₘ]
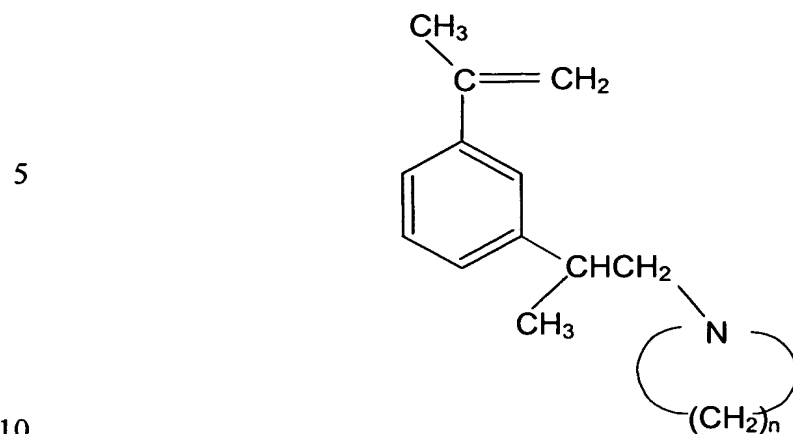
wherein n represents an integer from 0 to about 10, wherein m represents an integer from 0 to about 10, wherein x represents an integer from 1 to about 10, and wherein y represents an integer from 1 to about 10.

The present invention further discloses a process for

synthesizing an amino methyl styrene monomer which comprises: (1) reacting divinyl benzene with a cyclic amine in a reacting mixture in the presence of an alkyl lithium compound at a temperature which is within the range of -

5 80°C to 80°C to produce the amino ethyl styrene; and (2) deactivating the alkyl lithium compound by adding an alcohol or water to the reaction mixture containing the amino ethyl styrene. This process is preferable conducted at a temperature which is within the range of about -20°C

10 to about 50°C and is most preferable conducted at a temperature is within the range of about -10°C to about 25°C. The alkyl lithium compound is typically present at a level which is within the range of about 0.5 mole percent to about 5 mole percent, based upon the molar amount of

15 cyclic amine present. The alkyl lithium compound is preferably present at a level which is within the range of about 1 mole percent to about 4 mole percent and is more preferably present at a level which is within the range of about 1.5 mole percent to about 2.5 mole percent, based

20 upon the molar amount of cyclic amine present.

Detailed Description of the Invention

The functionalized monomers of this invention can be copolymerized into virtually any type of synthetic rubber.

25 In most cases the functionalized monomer will be copolymerized with at least one conjugated diolefin monomer. Optionally, other monomers that are copolymerizable with conjugated diolefin monomers, such as vinyl aromatic monomers, can also be included in the

30 polymerization. In any case, typically from about 0.1 phm (parts by weight by 100 parts by weight of monomers) to about 100 phm of the functionalized monomer will be included in the polymerization. More typically, from about

0.05 phm to about 10 phm of the functionalized monomer will
be included in the rubbery polymer. Good results can
normally be attained by including 0.1 phm to 5 phm of the
functionalized monomer in the rubbery polymer.

5   According to this invention, polymerization and
recovery of polymer are suitably carried out according to
various methods suitable for diene monomer polymerization
processes. This includes batchwise, semi-continuous, or
continuous operations under conditions that exclude air and
10   other atmospheric impurities, particularly oxygen and
moisture. The polymerization of the functionalized
monomers of the invention may also be carried out in a
number of different polymerization reactor systems,
including but not limited to bulk polymerization, vapor
15   phase polymerization, solution polymerization, suspension
polymerization, emulsion polymerization, and precipitation
polymerization systems. The commercially preferred methods
of polymerization are solution polymerization and emulsion
polymerization.

20   The polymerization reaction may use a free radical
initiator, a redox initiator, an anionic initiator, a
cationic initiator, or a Zeigler-Natta catalyst system.
The preferred initiation system depends upon the particular
monomers being polymerized and the desired characteristics
25   of the rubbery polymer being synthesized. In emulsion
polymerizations free radical initiators are typically
utilized. In solution polymerizations Zeigler-Natta
catalyst systems or anionic initiators, such as alkyl
lithium compounds, are typically employed to initiate the
30   polymerization. An advantage of free radical
polymerization is that reactions can typically be carried
out under less rigorous conditions than ionic
polymerizations. Free radical initiation systems also

exhibit a greater tolerance of trace impurities.

Examples of free radical initiators that are useful in the practice of the present invention are those known as "redox" initiators, such as combinations of chelated iron salts, sodium formaldehyde sulfoxylate, and organic hydroperoxides. Representative of organic hydroperoxides are cumene hydroperoxide, paramenthane hydroperoxide, and tertiary butyl hydroperoxide. Tertiary butyl hydroperoxide (t-BHP), tertiary butyl peracetate (t-BPA) and "azo" initiators, such as azobisiobutyronitrile (AIBN), are preferred.

The reaction temperature is typically maintained in the range of 0°C to 150°C. Temperatures between about 20 and 80°C are generally preferred. The reaction pressure is not critical. It is typically only sufficiently high to maintain liquid phase reaction conditions; it may be autogenic pressure, which will vary depending upon the components of the reaction mixture and the temperature, or it may be higher, e.g., up to 1000 psi.

In batch operations, the polymerization time of functionalized diene monomers can be varied as desired; it may vary, for example, from a few minutes to several days. Polymerization in batch processes may be terminated when monomer is no longer absorbed, or earlier, if desired, e.g., if the reaction mixture becomes too viscous. In continuous operations, the polymerization mixture may be passed through a reactor of any suitable design. The polymerization reactions in such cases are suitably adjusted by varying the residence time. Residence times vary with the type of reactor system and range, for example, from 10 to 15 minutes to 24 or more hours.

The concentration of monomer in the reaction mixture may vary upward from 5 percent by weight of the reaction

mixture, depending on the conditions employed; the range from 20 to 80 percent by weight is preferred.

The polymerization reactions according to this invention may be carried out in a suitable solvent that is liquid under the conditions of reaction and relatively inert. The solvent may have the same number of carbon atoms per molecule as the diene reactant or it may be in a different boiling range. Preferred as solvents are alkane and cycloalkane hydrocarbons. Suitable solvents are, for example, hexane, cyclohexane, methylcyclohexane, or various saturated hydrocarbon mixtures. Aromatic hydrocarbons such as benzene, toluene, isopropylbenzene, xylene, or halogenated aromatic compounds such as chlorobenzene, bromobenzene, or orthodichlorobenzene may also be employed. Other useful solvents include tetrahydrofuran and dioxane.

Conventional emulsion recipes may also be employed with the present invention; however, some restrictions and modifications may arise either from the polymerizable monomer itself, or the polymerization parameters. Ionic surfactants, known in the art, including sulfonate detergents and carboxylate, sulfate, and phosphate soaps are useful in this invention. The level of ionic surfactant is computed based upon the total weight of the organic components and may range from about 2 to 30 parts by weight of ionic surfactant per 100 parts by weight of organic components.

Preferably the polymerization is carried out to complete functionalized diene monomer conversion in order to incorporate essentially all of the polymerizable functional group-bearing monomer. Incremental addition, or a chain transfer agent, may be used in order to avoid excessive gel formation. Such minor modifications are within the skill of the artisan. After the polymerization

is complete, the polymer is recovered from a slurry or solution of the polymer. A simple filtration may be adequate to separate polymer from diluent. Other means for separating polymer from diluent may be employed. The

5 polymer may be treated, separately or while slurried in the reaction mixture, in order to separate residues. Such treatment may be with alcohols such as methanol, ethanol, or isopropanol, with acidified alcohols, or with other similar polar liquids. In many cases the polymers are

10 obtained in hydrocarbon solutions and the polymer can be recovered by coagulation with acidified alcohol, e.g., rapidly stirred methanol or isopropanol containing 2% hydrochloric acid. Following this initial coagulation,the polymers may be washed several more times in methanol.

15 The functionalized diene monomers according to the present invention may also be polymerized with one or more comonomers. Some adjustments in the polymerization recipe or reaction conditions may be necessary to obtain a satisfactory rate of polymer formation, depending on the

20 amount of functionalized monomer included and the other monomers involved. Examples of comonomers that are useful in the practice of this invention are diene monomers such as butadiene, isoprene, and hexadienes. One may, in addition to the diene monomers, use a vinyl monomer such as

25 styrene, α-methylstyrene, divinyl benzene, vinyl chloride, vinyl acetate, vinylidene chloride, methyl methacrylate, ethyl acrylate, vinylpyridine, acrylonitrile, methacrylonitrile, methacrylic acid, itaconic acid and acrylic acid. Mixtures of different functionalized monomers

30 and mixtures of different comonomers may be used. The monomer charge ratio by weight is normally from about 0.10/99.9 to 99.9/0.10 functionalized monomer to comonomer (including any additional vinyl monomer). A charge ratio

by weight of about 5/95 to about 80/20 is preferred with 10/90 to 40/60 the most preferred. According to one embodiment, the weight ratio of functionalized diene monomer to diene monomer to vinyl monomer may range from 5:75:20 to 95:5:0. Ratios will vary depending on the amount of chemical functionality desired to be incorporated and on the reactivity ratios of the monomers in the particular polymerization system used.

The functionalized monomers of this invention offer a unique ability to randomly copolymerize with conjugated diolefin monomers in solution polymerizations that are conducted at temperatures of 20°C or higher. The functionalized monomers of this invention can be incorporated into virtually any type of rubbery polymer that is capable of being made by solution polymerization with an anionic initiator or Zeigler-Natta type of catalyst. The polymerization employed in synthesizing the rubbery polymers will normally be carried out in a hydrocarbon solvent. Such hydrocarbon solvents are comprised of one or more aromatic, paraffinic or cycloparaffinic compounds. These solvents will normally contain from about 4 to about 10 carbon atoms per molecule and will be liquid under the conditions of the polymerization. Some representative examples of suitable organic solvents include pentane, isooctane, cyclohexane, methylcyclohexane, isohexane, n-heptane, n-octane, n-hexane, benzene, toluene, xylene, ethylbenzene, diethylbenzene, isobutylbenzene, petroleum ether, kerosene, petroleum spirits, petroleum naphtha, and the like, alone or in admixture.

In the solution polymerization, there will normally be from 5 to 30 weight percent monomers in the polymerization medium. Such polymerization media are, of course,

comprised of the organic solvent and monomers. In most cases, it will be preferred for the polymerization medium to contain from 10 to 25 weight percent monomers. It is generally more preferred for the polymerization medium to contain 15 to 20 weight percent monomers.

The synthetic rubbers made by the process of this invention can be made by random copolymerization of the functionalized monomer with a conjugated diolefin monomer or by the random terpolymerization of the functionalized monomer with a conjugated diolefin monomer and a vinyl aromatic monomer. It is, of course, also possible to make such rubbery polymers by polymerizing a mixture of conjugated diolefin monomers with one or more ethylenically unsaturated monomers, such as vinyl aromatic monomers. The conjugated diolefin monomers which can be utilized in the synthesis of rubbery polymers which can be coupled in accordance with this invention generally contain from 4 to 12 carbon atoms. Those containing from 4 to 8 carbon atoms are generally preferred for commercial purposes. For similar reasons, 1,3-butadiene and isoprene are the most commonly utilized conjugated diolefin monomers. Some additional conjugated diolefin monomers that can be utilized include 2,3-dimethyl-1,3-butadiene, piperylene, 3-butyl-1,3-octadiene, 2-phenyl-1,3-butadiene, and the like, alone or in admixture.

Some representative examples of ethylenically unsaturated monomers that can potentially be polymerized into rubbery polymers that contain the functionalized monomers of this invention include alkyl acrylates, such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate and the like; vinylidene monomers having one or more terminal $CH_2=CH-$ groups; vinyl aromatics such as styrene, α-methylstyrene, bromostyrene, chlorostyrene,

fluorostyrene and the like; α-olefins such as ethylene, propylene, 1-butene and the like; vinyl halides, such as vinylbromide, chloroethane (vinylchloride), vinylfluoride, vinyliodide, 1,2-dibromoethene, 1,1-dichloroethene

5   (vinylidene chloride), 1,2-dichloroethene and the like; vinyl esters, such as vinyl acetate; α,β-olefinically unsaturated nitriles, such as acrylonitrile and methacrylonitrile; α,β-olefinically unsaturated amides, such as acrylamide, N-methyl acrylamide, N,N-

10   dimethylacrylamide, methacrylamide and the like.

Rubbery polymers which are copolymers of one or more diene monomers with one or more other ethylenically unsaturated monomers will normally contain from about 50 weight percent to about 99 weight percent conjugated

15   diolefin monomers and from about 1 weight percent to about 50 weight percent of the other ethylenically unsaturated monomers in addition to the conjugated diolefin monomers. For example, copolymers of conjugated diolefin monomers with vinylaromatic monomers, such as styrene-butadiene

20   rubbers which contain from 50 to 95 weight percent conjugated diolefin monomers and from 5 to 50 weight percent vinylaromatic monomers, are useful in many applications.

Vinyl aromatic monomers are probably the most

25   important group of ethylenically unsaturated monomers which are commonly incorporated into polydiene rubbers. Such vinyl aromatic monomers are, of course, selected so as to be copolymerizable with the conjugated diolefin monomers being utilized. Generally, any vinyl aromatic monomer

30   which is known to polymerize with organolithium initiators can be used. Such vinyl aromatic monomers typically contain from 8 to 20 carbon atoms. Usually, the vinyl aromatic monomer will contain from 8 to 14 carbon atoms.

The most widely used vinyl aromatic monomer is styrene.
Some examples of vinyl aromatic monomers that can be
utilized include styrene, 1-vinylnaphthalene, 2-
vinylnaphthalene, α-methylstyrene, 4-phenylstyrene, 3-
5   methylstyrene and the like.

      Some representative examples of rubbery polymers that
can be functionalized with the functionalized monomers of
this invention include polybutadiene, polyisoprene,
styrene-butadiene rubber (SBR), α-methylstyrene-butadiene
10   rubber, α-methylstyrene-isoprene rubber, styrene-isoprene-
butadiene rubber (SIBR), styrene-isoprene rubber (SIR),
isoprene-butadiene rubber (IBR), α-methylstyrene-isoprene-
butadiene rubber and α-methylstyrene-styrene-isoprene-
butadiene rubber. In cases where the rubbery polymer is
15   comprised of repeat units that are derived from two or more
monomers, the repeat units which are derived from the
different monomers, including the functionalized monomers,
will normally be distributed in an essentially random
manner. The repeat units that are derived from the
20   monomers differ from the monomer in that a double bond is
normally consumed in by the polymerization reaction.

      The rubbery polymer can be made by solution
polymerization in a batch process by in a continuous
process by continuously charging at least one conjugated
25   diolefin monomer, the functionalized monomer, and any
additional monomers into a polymerization zone. The
polymerization zone will typically be a polymerization
reactor or a series of polymerization reactors. The
polymerization zone will normally provide agitation to keep
30   the monomers, polymer, initiator, and modifier well
dispersed throughout the organic solvent the polymerization
zone. Such continuous polymerizations are typically
conducted in a multiple reactor system. The rubbery

polymer synthesized is continuously withdrawn from the polymerization zone. The monomer conversion attained in the polymerization zone will normally be at least about 85 percent. It is preferred for the monomer conversion to be

5   at least about 90 percent.

The polymerization will be initiated with an anionic initiator, such as an alkyl lithium compound, or a Zeigler-Natta catalyst. The alkyl lithium compounds that can be used will typically contain from 1 to about 8 carbon atoms,

10   such as n-butyl lithium,

The amount of the lithium initiator utilized will vary with the monomers being polymerized and with the molecular weight that is desired for the polymer being synthesized. However, as a general rule, from 0.01 to 1 phm (parts per

15   100 parts by weight of monomer) of the lithium initiator will be utilized. In most cases, from 0.01 to 0.1 phm of the lithium initiator will be utilized with it being preferred to utilize 0.025 to 0.07 phm of the lithium initiator.

20   The polymerization process of this invention is normally conducted in the presence of polar modifiers, such as alkyltetrahydrofurfuryl ethers. Some representative examples of specific polar modifiers that can be used include methyltetrahydrofurfuryl ether,

25   ethyltetrahydrofurfuryl ether, propyltetrahydrofurfuryl ether, butyltetrahydrofurfuryl ether, hexyltetrahydrofurfuryl ether, octyltetrahydrofurfuryl ether, dodecyltetrahydrofurfuryl ether, diethyl ether, di-n-propyl ether, diisopropyl ether, di-n-butyl ether,

30   tetrahydrofuran, dioxane, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, triethylene glycol dimethyl ether, trimethylamine, triethylamine, N,N,N',N'-

tetramethylethylenediamine, N-methyl morpholine, N-ethyl morpholine, or N-phenyl morpholine.

The polar modifier will typically be employed at a level wherein the molar ratio of the polar modifier to the lithium initiator is within the range of about 0.01:1 to about 5:1. The molar ratio of the polar modifier to the lithium initiator will more typically be within the range of about 0.1:1 to about 4:1. It is generally preferred for the molar ratio of polar modifier to the lithium initiator to be within the range of about 0.25:1 to about 3:1. It is generally most preferred for the molar ratio of polar modifier to the lithium initiator to be within the range of about 0.5:1 to about 3:2.

The polymerization can optionally be conducted utilizing an oligomeric oxolanyl alkane as the modifier. Such oligomeric oxolanyl alkanes will typically be of a structural formula selected from the group consisting of:

(a)

$$R_3 \underset{R_5}{\overset{O}{\bigcirc}} \underset{R_6}{\quad} \left[\overset{R_1}{\underset{R_2}{C}} \quad \underset{R_5}{\overset{O}{\bigcirc}} \underset{R_6}{\quad} \right]_n R_4$$

and

(b)

$$\left[\underset{R_5}{\overset{O}{\bigcirc}} \underset{R_6}{\quad} \left[\overset{R_1}{\underset{R_2}{C}} \quad \underset{R_5}{\overset{O}{\bigcirc}} \underset{R_6}{\quad} \right] \overset{R_1}{\underset{R_2}{C}} \right]_m$$

wherein n represents an integer from 1 to 5, wherein m
represents an integer from 3 to 5, wherein R_1, R_2, R_3, R_4,
R_5, and R_6 can be the same or different, and wherein R_1, R_2,
R_3, R_4, R_5, and R_6 represent a member selected from the group
consisting of hydrogen atoms and alkyl groups containing
from 1 to about 8 carbon atoms. It is typically preferred
for R_1, R_2, R_3, R_4, R_5, and R_6 represent a member selected
from the group consisting of hydrogen atoms and alkyl
groups containing from 1 to 4 carbon atoms.

The polymerization will also be conducted in the
presence of an alkali metal alkoxide. The alkali metal
alkoxide employed will typically be of the structural
formula: M-O-R wherein M represents an alkali metal and
wherein R represents an alkyl group (including cycloalkyl
groups), an aryl group, an alkaryl group, or an arylalkyl
groug. The alkali metal will normally be a metal from
Group I of the Periodic Table with lithium, sodium and
potassium being preferred. Some representative examples of
alkali metal alkoxides that can be used include: lithium
methoxide, lithium ethoxide, lithium isopropoxide, lithium

n-butoxide, lithium sec-butoxide, lithium t-butoxide, lithium 1,1-dimethylpropoxide, lithium 1,2-dimethylpropoxide, lithium 1,1-dimethylbutoxide, lithium 1,10-dimethylpentoxide, lithium 2-ethylhexanoxide, lithium

5 1-methylheptoxide, lithium phenoxide, lithium p-methylphenoxide, lithium p-octylphenoxide, lithium p-nonylphenoxide, lithium p-dodecylphenoxide, lithium α-naphthoxide, lithium β-naphthoxide, lithium o-methoxyphenoxide, lithium o-metnoxyphenoxide, lithium m-

10 methoxyphenoxide, lithium p-methoxyphenoxide, lithium o-ethoxyphenoxide, lithium 4-methoxy-1-naphthoxide, sodium methoxide, sodium ethoxide, sodium isopropoxide, sodium n-butoxide, sodium sec-butoxide, sodium t-butoxide, sodium 1,1-dimethylpropoxide, sodium 1,2-dimethylpropoxide, sodium

15 1,1-dimethylbutoxide, sodium 1,10-dimethylpentoxide, sodium 2-ethylhexanoxide, sodium 1-methylheptoxide, sodium phenoxide, sodium p-methylphenoxide, sodium p-octylphenoxide, sodium p-nonylphenoxide, sodium p-dodecylphenoxide, sodium α-naphthoxide, sodium β-

20 naphthoxide, sodium o-methoxyphenoxide, sodium o-metnoxyphenoxide, sodium m-methoxyphenoxide, sodium p-methoxyphenoxide, sodium o-ethoxyphenoxide, sodium 4-methoxy-1-naphthoxide, potassium methoxide, potassium ethoxide, potassium isopropoxide, potassium n-butoxide,

25 potassium sec-butoxide, potassium t-butoxide, potassium 1,1-dimethylpropoxide, potassium 1,2-dimethylpropoxide, potassium 1,1-dimethylbutoxide, potassium 1,10-dimethylpentoxide, potassium 2-ethylhexanoxide, potassium 1-methylheptoxide, potassium phenoxide, potassium p-

30 methylphenoxide, potassium p-octylphenoxide, potassium p-nonylphenoxide, potassium p-dodecylphenoxide, potassium α-naphthoxide, potassium β-naphthoxide, potassium o-methoxyphenoxide, potassium o-metnoxyphenoxide, potassium

m-methoxyphenoxide, potassium p-methoxyphenoxide, potassium
o-ethoxyphenoxide, potassium 4-methoxy-1-naphthoxide, and
the like.

It is preferred for the alkali metal alkoxide to be an
alkali metal salt of a cyclic alcohol. The metal salt of
the cyclic alcohol will typically be a Group Ia metal salt.
Lithium, sodium, potassium, rubidium, and cesium salts are
representative examples of such salts with lithium, sodium,
and potassium salts being preferred. Sodium salts are
typically the most preferred. The cyclic alcohol can be
mono-cyclic, bi-cyclic or tri-cyclic and can be aliphatic
or aromatic. They can be substituted with 1 to 5
hydrocarbon moieties and can also optionally contain
hetero-atoms. For instance, the metal salt of the cyclic
alcohol can be a metal salt of a di-alkylated cyclohexanol,
such as 2-isopropyl-5-methylcyclohexanol or 2-t-butyl-5-
methylcyclohexanol. These salts are preferred because they
are soluble in hexane. Metal salts of disubstituted
cyclohexanol are highly preferred because they are soluble
in hexane and provide similar modification efficiencies to
sodium t-amylate. Sodium mentholate is the most highly
preferred metal salt of a cyclic alcohol that can be
employed in the practice of this invention. Metal salts of
thymol can also be utilized. The metal salt of the cyclic
alcohol can be prepared by reacting the cyclic alcohol
directly with the metal or another metal source, such as
sodium hydride, in an aliphatic or aromatic solvent.
Some representative examples of alcohols which can be
utilized in preparing the lithium alkoxide include t-
butanol, sec-butanol, cyclohexanol, octanol, 2-
ethylhexanol, p-cresol, m-cresol, nonylphenol, hexylphenol,
tetrahydrofuryl alcohol, furfuryl alcohol, and
tetrahydrofurfuryl, and the like.

The molar ratio of the alkali metal alkoxide to the lithium initiator will typically be within the range of about 0.001:1 to about 2:1. The molar ratio of the alkali metal alkoxide to the lithium initiator will more typically

5   be within the range of about 0.005:1 to about 1:1. The molar ratio of the alkali metal alkoxide to the lithium initiator will preferably be within the range of about 0.008:1 to about 0.3:1.

The polymerization temperature utilized can vary over

10   a broad range of from about -20°C to about 180°C. In most cases, a polymerization temperature within the range of about 30°C to about 125°C will be utilized. It is typically preferred for the polymerization temperature to be within the range of about 45°C to about 100°C. It is

15   typically most preferred for the polymerization temperature to be within the range of about 60°C to about 90°C. The pressure used will normally be sufficient to maintain a substantially liquid phase under the conditions of the polymerization reaction.

20   The polymerization is conducted for a length of time sufficient to permit substantially complete polymerization of monomers. In other words, the polymerization is normally carried out until high conversions of at least about 85 percent are attained. The polymerization is then

25   terminated by the addition of an agent, such as an alcohol, a terminating agent, or a coupling agent. For example, a tin halide and/or silicon halide can be used as a coupling agent. The tin halide and/or the silicon halide are continuous added in cases where asymmetrical coupling is

30   desired. This continuous addition of tin coupling agent and/or the silicon coupling agent is normally done in a reaction zone separate from the zone where the bulk of the polymerization is occurring. The coupling agents will

normally be added in a separate reaction vessel after the desired degree of conversion has been attained. The coupling agents can be added in a hydrocarbon solution, e.g., in cyclohexane, to the polymerization admixture with
5   suitable mixing for distribution and reaction. In other words, the coupling will typically be added only after a high degree of conversion has already been attained. For instance, the coupling agent will normally be added only after a monomer conversion of greater than about 85 percent
10 has been realized. It will typically be preferred for the monomer conversion to reach at least about 90 percent before the coupling agent is added.

The tin halides used as coupling agents will normally be tin tetrahalides, such as tin tetrachloride, tin
15 tetrabromide, tin tetrafluoride or tin tetraiodide. However, tin trihalides can also optionally be used. Polymers coupled with tin trihalides having a maximum of three arms. This is, of course, in contrast to polymers coupled with tin tetrahalides which have a maximum of four
20 arms. To induce a higher level of branching, tin tetrahalides are normally preferred. As a general rule, tin tetrachloride is most preferred.

The silicon coupling agents that can be used will normally be silicon tetrahalides, such as silicon
25 tetrachloride, silicon tetrabromide, silicon tetrafluoride or silicon tetraiodide. However, silicon trihalides can also optionally be used. Polymers coupled with silicon trihalides having a maximum of three arms. This is, of course, in contrast to polymers coupled with silicon
30 tetrahalides which have a maximum of four arms. To induce a higher level of branching, silicon tetrahalides are normally preferred. As a general rule, silicon tetrachloride is most preferred of the silicon coupling

agents.

A combination of a tin halide and a silicon halide can optionally be used to couple the rubbery polymer. By using such a combination of tin and silicon coupling agents improved properties for tire rubbers, such as lower hysteresis, can be attained. It is particularly desirable to utilize a combination of tin and silicon coupling agents in tire tread compounds that contain both silica and carbon black. In such cases, the molar ratio of the tin halide to the silicon halide employed in coupling the rubbery polymer will normally be within the range of 20:80 to 95:5. The molar ratio of the tin halide to the silicon halide employed in coupling the rubbery polymer will more typically be within the range of 40:60 to 90:10. The molar ratio of the tin halide to the silicon halide employed in coupling the rubbery polymer will preferably be within the range of 60:40 to 85:15. The molar ratio of the tin halide to the silicon halide employed in coupling the rubbery polymer will most preferably be within the range of 65:35 to 80:20.

Broadly, and exemplary, a range of about 0.01 to 4.5 milliequivalents of tin coupling agent (tin halide and silicon halide) is employed per 100 grams of the rubbery polymer. It is normally preferred to utilize about 0.01 to about 1.5 milliequivalents of the coupling agent per 100 grams of polymer to obtain the desired Mooney viscosity. The larger quantities tend to result in production of polymers containing terminally reactive groups or insufficient coupling. One equivalent of tin coupling agent per equivalent of lithium is considered an optimum amount for maximum branching. For instance, if a mixture tin tetrahalide and silicon tetrahalide is used as the coupling agent, one mole of the coupling agent would be

utilized per four moles of live lithium ends. In cases where a mixture of tin trihalide and silicon trihalide is used as the coupling agent, one mole of the coupling agent will optimally be utilized for every three moles of live

5   lithium ends. The coupling agent can be added in a hydrocarbon solution, e.g., in cyclohexane, to the polymerization admixture in the reactor with suitable mixing for distribution and reaction.

After the coupling has been completed, a tertiary

10   chelating alkyl 1,2-ethylene diamine or a metal salt of a cyclic alcohol can optionally be added to the polymer cement to stabilize the coupled rubbery polymer. The tertiary chelating amines that can be used are normally chelating alkyl diamines of the structural formula:

15

$$R'\text{---}\underset{\underset{R''}{|}}{N}\left[\text{---}A\text{---}\underset{\underset{R'''}{|}}{N}\right]_{n}\text{---}R''''$$

20   wherein n represents an integer from 1 to about 6, wherein A represents an alkylene group containing from 1 to about 6 carbon atoms and wherein R', R'', R''' and R'''' can be the same or different and represent alkyl groups containing from 1 to about 6 carbon atoms. The alkylene group A is of

25   the formula $-(-CH_2-)_m$ wherein m is an integer from 1 to about 6. The alkylene group will typically contain from 1 to 4 carbon atoms (m will be 1 to 4) and will preferably contain 2 carbon atoms. In most cases, n will be an integer from 1 to about 3 with it being preferred for n to

30   be 1. It is preferred for R', R'', R''' and R'''' to represent alkyl groups which contain from 1 to 3 carbon atoms. In most cases, R', R'', R''' and R'''' will represent methyl groups.

In most cases, from about 0.01 phr (parts by weight per 100 parts by weight of dry rubber) to about 2 phr of the chelating alkyl 1,2-ethylene diamine or metal salt of the cyclic alcohol will be added to the polymer cement to

5   stabilize the rubbery polymer. Typically, from about 0.05 phr to about 1 phr of the chelating alkyl 1,2-ethylene diamine or metal salt of the cyclic alcohol will be added. More typically, from about 0.1 phr to about 0.6 phr of the chelating alkyl 1,2-ethylene diamine or the metal salt of

10   the cyclic alcohol will be added to the polymer cement to stabilize the rubbery polymer.

The terminating agents that can be used to stop the polymerization and to "terminate" the living rubbery polymer include tin monohalides, silicon monohalides,

15   N,N,N',N'-tetradialkyldiamino-benzophenones (such as tetramethyldiaminobenzophenone and the like), N,N-dialkylamino-benzaldehydes (such as dimethylaminobenzaldehyde and the like), 1,3-dialkyl-2-imidazolidinones (such as 1,3-dimethyl-2-imidazolidinone

20   and the like), 1-alkyl substituted pyrrolidinones; 1-aryl substituted pyrrolidinones, dialkyl- dicycloalkyl-carbodiimides containing from about 5 to about 20 carbon atoms, and dicycloalkyl-carbodiimides containing from about 5 to about 20 carbon atoms.

25   After the termination step, and optionally the stabilization step, has been completed, the rubbery polymer can be recovered from the organic solvent. The coupled rubbery polymer can be recovered from the organic solvent and residue by means such as chemical (alcohol)

30   coagulation, thermal desolventization, or other suitable method. For instance, it is often desirable to precipitate the rubbery polymer from the organic solvent by the addition of lower alcohols containing from about 1 to about

4 carbon atoms to the polymer solution. Suitable lower
alcohols for precipitation of the rubber from the polymer
cement include methanol, ethanol, isopropyl alcohol,
normal-propyl alcohol and t-butyl alcohol. The utilization
5   of lower alcohols to precipitate the rubbery polymer from
the polymer cement also "terminates" any remaining living
polymer by inactivating lithium end groups. After the
coupled rubbery polymer is recovered from the solution,
steam-stripping can be employed to reduce the level of
10   volatile organic compounds in the coupled rubbery polymer.
Additionally, the organic solvent can be removed from the
rubbery polymer by drum drying, extruder drying, vacuum
drying, and the like.

The polymers of the present invention can be used
15   alone or in combination with other elastomers to prepare an
rubber compounds, such as a tire treadstock, sidewall stock
or other tire component stock compounds. In a tire of the
invention, at least one such component is produced from a
vulcanizable elastomeric or rubber composition. For
20   example, the rubbery polymer made by the process of this
invention can be blended with any conventionally employed
treadstock rubber which includes natural rubber, synthetic
rubber and blends thereof. Such rubbers are well known to
those skilled in the art and include synthetic polyisoprene
25   rubber, styrene/butadiene rubber (SBR), polybutadiene,
butyl rubber, Neoprene, ethylene/propylene rubber,
ethylene/propylene/diene rubber (EPDM),
acrylonitrile/butadiene rubber (NBR), silicone rubber, the
fluoroelastomers, ethylene acrylic rubber, ethylene vinyl
30   acetate copolymer (EVA), epichlorohydrin rubbers,
chlorinated polyethylene rubbers, chlorosulfonated
polyethylene rubbers, hydrogenated nitrile rubber,
tetrafluoroethylene/propylene rubber and the like.

When the rubbery polymers made by the process of the present invention are blended with conventional rubbers, the amounts can vary widely such as between 10 and 99 percent by weight. In any case, tires made with synthetic

5 rubbers that are synthesized utilizing the technique of this invention exhibit decreased rolling resistance. The greatest benefits are realized in cases where the tire tread compound is made with the rubbery polymer synthesized utilizing the technique of this invention. However,

10 benefits can also by attained in cases where at least one structural element of the tire, such as subtread, sidewalls, body ply skim, or bead filler, is comprised of the rubbery.

The synthetic rubbers made in accordance with this

15 invention can be compounded with carbon black in amounts ranging from about 5 to about 100 phr (parts by weight per 100 parts by weight of rubber), with about 5 to about 80 phr being preferred ,and with about 40 to about 70 phr being more preferred. The carbon blacks may include any of

20 the commonly available, commercially-produced carbon blacks but those having a surface area (EMSA) of at least 20 m^2/g and more preferably at least 35 m^2/g up to 200 m^2/g or higher are preferred. Surface area values used in this application are those determined by ASTM test D-1765 using

25 the cetyltrimethyl-ammonium bromide (CTAB) technique. Among the useful carbon blacks are furnace black, channel blacks and lamp blacks. More specifically, examples of the carbon blacks include super abrasion furnace (SAF) blacks, high abrasion furnace (HAF) blacks, fast extrusion furnace

30 (FEF) blacks, fine furnace (FF) blacks, intermediate super abrasion furnace (ISAF) blacks, semi-reinforcing furnace (SRF) blacks, medium processing channel blacks, hard processing channel blacks and conducting channel blacks.

Other carbon blacks which may be utilized include acetylene blacks. Mixtures of two or more of the above blacks can be used in preparing the carbon black products of the invention. Typical values for surface areas of usable
5   carbon blacks are summarized in the following table.

<div align="center">Carbon Black</div>

ASTM Designation (D-1765-82a)	Surface Area (D-3765)
N-110	126 m^2/g
N-220	111 m^2/g
N-330	83 m^2/g
N-339	95 m^2/g
N-550	42 m^2/g
N-660	35 m^2/g

The carbon blacks utilized in the preparation of rubber compounds may be in pelletized form or an unpelletized flocculent mass. Preferably, for more uniform mixing, unpelletized carbon black is preferred. The
20   reinforced rubber compounds can be cured in a conventional manner with about 0.5 to about 4 phr of known vulcanizing agents. For example, sulfur or peroxide-based curing systems may be employed. For a general disclosure of suitable vulcanizing agents one can refer to Kirk-Othmer,
25   Encyclopedia of Chemical Technology, 3rd ed., Wiley Interscience, N.Y. 1982, Vol. 20, pp. 365-468, particularly "Vulcanization Agents and Auxiliary Materials" pp. 390-402. Vulcanizing agents can, of curse, be used alone or in combination. Vulcanizable elastomeric or rubber
30   compositions can be prepared by compounding or mixing the polymers thereof with carbon black and other conventional rubber additives such as fillers, plasticizers, antioxidants, curing agents and the like, using standard

rubber mixing equipment and procedures and conventional amounts of such additives.

The functionalized styrene monomer can be synthesized by (1) reacting a primary or secondary amine with an organolithium compound to produce a lithium amide, and (2) reacting the lithium amide with divinylbenzene or diisopropenyl benzene to produce the functionalized styrene monomer. It is preferred to utilize a secondary amine in the first step. This procedure can be depicted as follows:

Where X⁺ = Na⁺ or Li⁺

A process for synthesizing an amino ethyl styrene monomer which comprises: (1) reacting divinyl benzene with a cyclic amine in a reacting mixture in the presence of an alkyl lithium compound at a temperature which is within the range of -80°C to 80°C to produce the amino ethyl styrene; and (2) deactivating the alkyl lithium compound by adding an alcohol or water to the reaction mixture containing the amino ethyl styrene.

Functionalized monomers that contain cyclic amines can also be made by the same reaction scheme wherein a cyclic secondary amine is employed in the first step of the reaction. This reaction scheme can be depicted as follows:

5

10

Where $X^+ = Na^+$ or Li^+

In another embodiment of this invention a

15   functionalized monomer can be synthesized by a process that
comprises (1) reacting a secondary amine with a 2,3-
dihalopropene to produce a vinyl halide containing
secondary amine having a structural formula selected from
the group consisting of

20

(a)

25

wherein R and R' can be the same or different and represent
allyl, alkoxyl or alkyl groups containing from 1 to about
10 carbon atoms, and wherein X represents a halogen atom,
and

30

(b)

wherein m represents an integer from 4 to about 10, and
wherein X represents a halogen atom; and (2) reacting the
vinyl halide containing secondary amine with a vinyl
magnesium halide to produce the monomer, wherein the
monomer has a structural formula selected from the group
consisting of

(a)

wherein R and R' can be the same or different and represent
allyl groups, alkoxyl groups, tetra alkyl silyl groups, or
alkyl groups containing from 1 to about 10 carbon atoms,
and

(b)

wherein m represents an integer from about 4 to about 10.

Such a reaction scheme can be depicted as follows:

In the first step of this reaction scheme a secondary
5   cyclic amine is reacted with a 2,3-dihalopropene (2,3-
bromopropene is shown above). This step is typically
conducted in an organic solvent, such as diethyl ether, at
a temperature which is within the range of about -20°C to
about 60°C, and is preferable conducted at a temperature
10   which is within the range of 0°C to about 30°C. The same
product above can be made in aqueous sodium hydroxide
solution containing one mole of the cyclic amine followed
by dropwise addition of the 2,3-dihalo-1-propene followed
by ether extraction and vacuum distillation to recover the
15   product. As can be seen, this results in the production of
a vinyl halide containing secondary amine.

In the second step of the process the vinyl halide
containing secondary amine is reacted with a vinyl
magnesium halide to produce the functionalized monomer.

The second step is conducted in a polar organic solvent, such as tetrahydrofuran or diethyl ether. The second step is also conducted at a temperature that is within the range of about -20°C to about 60°C, and is preferable conducted

5   at a temperature which is within the range of 0°C to about 30°C.

This invention is illustrated by the following examples that are merely for the purpose of illustration and are not to be regarded as limiting the scope of the

10   invention or the manner in which it can be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

Example 1

15   In this experiment 2-(N-hexamethyleneimino)-methyl 1,3-butadiene was synthesized utilizing the technique of this invention. In the procedure used a solution of 2,3-dibromopropane (0.1 mol) in ethyl ether was slowly added to a solution of hexamethyleneimine (0.4 mol) in an aqueous

20   30% sodium hydroxide solution at 60°C. The reaction mixture was stirred overnight at room temperature. The next day the organic layer was collected using a separatory funnel and extracted with diethyl ether. The organic layer was subsequently washed with water two times. After drying

25   with sodium sulfate, the filtrate was evaporated and the resulting residue was distilled to yield 2-bromo-3-(N-hexamethyleneimino)propene. The boiling point and yield of the product were determined to be 65-68°C at 30 mm-Hg. The yield was determined to be 60%. The molecular structure of

30   2-bromo-3-(N-hexamethylene-imino)propene was verified by proton NMR.

Vinyl magnesium bromide in tetrahydrofuran (THF; 0.085 mol) was added dropwise to a flask containing the 2-bromo-

3-(N-hexamethylene-imino)propene (0.056 mol) in the presence of [1,3-bis(diphenylphosphino) propane] dichloronickel(II) (0.21 mol) at 0°C. After stirring for 24 hours at room temperature, the hydrolysis of the reaction mixture by saturated ammonium chloride solution was carried out and followed by extraction with diethyl ethyl three times. The organic material was dried by sodium sulfate and then filtered. After evaporating the solvent, the residue was distilled to give a colorless liquid of 2-(N-hexa-methyleneimino)-methyl 1,3-butadiene. The boiling point and yield were -114°C at 30 mm-Hg and 60%, respectively. The molecular structure of the resulting product was verified by proton NMR.

Example 2

The preparation of 2-(N,N-diethylamino)-methyl-1,3-butadiene is described in this example. The procedure described in Example 1 was utilized except that N,N-diethylamine was used in place of hexamethyleneimine. The yield for the intermediate product, 2-bromo-3-(N,N-diethylamino)propene was 98%. The boiling point and yield of the final product, 2-(N,N-diethylamino)-methyl-1,3-butadine was determined to be 112-114°C at 30 mm-Hg and 50%, respectively.

Examples 3-5

In these experiments 2-(N-pyrrolidino)-methyl-1,3-butadiene, 2-(N-morpholino)-methyl-1,3-butadiene, and 2-(N-piperidino)-methyl-1,3-butadiene were synthesized utilizing a procedure that is similar to the one described in Example 1 except that pyrrolidine, morpholine and piperidine were used in place of the hexamethyleneimine.

Example 6

In this experiment, a 25/75 SBR containing 1% of hexamethyleneimine (HMI) functional groups was prepared. 2350 g of a silica/alumina/molecular sieve dried premix containing 19.50 weight percent styrene and 1,3-butadiene in hexanes was charged into a one-gallon (3.8 liters) reactor. The styrene to 1,3-butadiene ratio was 25:75. 4.6 grams of a neat 2-(N-hexamethyleneimino)-methyl 1,3-butadiene was added to the reactor. Then, 2.9 ml of 1 M solution of N,N,N',N'-tetramethyethylenediamine (TMEDA) and 2.3 ml of 1.6 M n-butyl lithium (n-BuLi) in hexanes were added to the reactor, respectively. The polymerization was carried out at 70°C for 90 minutes. The GC analysis of the residual monomer contained in the polymerization mixture indicated that the all monomers were consumed at this time, the polymer cement was then shortstopped with ethanol and then removed from the reactor and stabilized with 1 phm of antioxidant. After evaporating hexanes, the resulting polymer was dried in a vacuum oven at 50°C.

The styrene-butadiene rubber (SBR) produced was determined to have a glass transition temperature (Tg) at -33°C. It was also determined to have a microstructure which contained 41 percent 1,2-polybutadiene units, 34 percent 1,4-polybutadiene units and 25 percent random polystyrene units. It also contained about 1 weight percent of HMI units. The Mooney viscosity (ML-4) at 100°C for this SBR was determined to be 27. The GPC data of this polymer was also determined to have a Mn of 129,000 and Mw of 136,000. The polydispersity (Mw/Mn) was 1.05. The HMI functionality of the resulting SBR was verified via a HPLC-GPEC (Gradient polymer elution chromatography) method using Novapak C18 column using a mixture of acetonitrile/THF as solvent. As determined by GPEC method, 93% of this polymer

contains HMI functional groups.

Examples 7-8

In these examples, 25/75 SBRs containing 0.25 and 0.5
weight percent of 2-(N-hexamethyleneimino)-methyl 1,3-
butadiene were prepared using the procedures described in
Example 6 except that 1.2 and 2.3 grams of 2-(N-
hexamethyleneimino)-methyl 1,3-butadiene, respectively were
added to the premix prior to polymerization. The
characterization data of these two polymers are listed in
Table 1.

Example 9

In the example, a tin coupled 25/75 SBR containing 0.5
weight percent of 2-(N-hexamethyleneimino)-methyl 1,3-
butadiene was prepared. 2350 g of a
silica/alumina/molecular sieve dried premix containing
19.50 weight percent styrene and 1,3-butadiene in hexanes
was charged into a one-gallon (3.8 liters) reactor. The
styrene to 1,3-butadiene ratio was 25:75. 2.3 grams of a
neat 2-(N-hexamethyleneimino)-methyl 1,3-butadiene was
added to the reactor. 2.9 ml of 1 M solution of N,N,N',
N'-tetramethyethylenediamine (TMEDA) and 2.3 ml of 1.6 M n-
butyl lithium (n-BuLi) in hexanes were added to the
reactor, respectively. The polymerization was carried out
at 70 ^{0}C for 90 minutes. The GC analysis of the residual
monomer contained in the polymerization mixture indicated
that the all monomers were consumed at this time. 0.9 ml
of a 1 M solution of tin tetrachloride in hexanes was then
added to the polymerization mixture. The coupling reaction
was allowed to proceed at 70^{0}C for 30 minutes. The coupling
efficiency was 69%. The characterization data of this
coupled and HMI functionalized polymer are also listed in

Table 1.

Comparative Example 10

In this example, a control 25/75 SBR containing 0
weight percent of 2-(N-hexamethyleneimino)-methyl 1,3-
butadiene was prepared using the procedures described in
Example 6 except no 2-(N-hexamethyleneimino)-methyl 1,3-
butadiene was used. The characterization data of this
polymer are also included in Table 1.

TABLE 1

Example No.	wt % HMI-Monomer	Coupler	Tg (^{0}C)	ML-4	GPC Mn	Mw	Mw/Mn
10	0	None	-33	23	137,000	139,000	1.02
7	0.25	None	-36	21	126,000	128,000	1.01
8	0.50	None	-32	27	139,000	142,000	1.03
6	1.00	None	-33	27	129,000	136,000	1.05
9	0.50	SnCl4	-32	83	677,000	812,000	1.20 (42%)
					329,000	335,000	1.02 (27%)
					145,000	155,000	1.06 (31%)

Example 11

In this example, a 25/75 SBR containing 0.5 weight
percent of 2-(N-hexamethyleneimino)-methyl 1,3-butadiene
was prepared using the procedures described in Example 6
except that 2.3 grams of 2-(N-hexamethyleneimino)-methyl
1,3-butadiene was pre-reacted with n-BuLi in the presence
of TMEDA. The pre-reacted n-BuLi containing HMI functional
groups was then used as the catalyst to initiate the
polymerization. The characterization data of this polymer
are listed in Table 2.

Examples 12-13

In these examples, 25/75 SBRs containing 0.1 and 0.25%
weight percent of 2-(N-hexamethyleneimino)-methyl 1,3-
butadiene were prepared using the procedures described in
Example 11 except that 0.5 and 1.2 grams of 2-(N-

hexamethyleneimino)-methyl 1,3-butadiene were pre-reacted with n-BuLi in the presence of TMEDA. The characterization data of this polymer are listed in Table 2.

5

Example 14

In this example, a 25/75 SBR containing 0.5 weight percent of 2-(N-hexamethyleneimino)-methyl 1,3-butadiene were prepared using the procedures described in Example 6 except that 4.6 grams of 2-(N-hexamethyleneimino)-methyl

10   1,3-butadiene was diluted with 10.8 ml of dried hexane and added sequentially in 5 equal portions (3 ml each) to the polymerization mixture at 0, 5, 15, 30 and 90 minutes time periods. The total polymerization time was 100 minutes. The characterization data of this polymer are listed in

15   Table 2.

Examples 15-16

In these examples, 25/75 SBRs containing 0.1 and 0.25 weight percent of 2-(N-hexamethyleneimino)-methyl 1,3-

20   butadiene were prepared using the procedures described in Example 14 except that 0.5 and 1.2 grams of 2-(N-hexamethyleneimino)-methyl 1,3-butadiene were added sequentially to the polymerization mixture as indicated in Example 14. The characterization data of this polymer are

25   listed in Table 2.

Example 17

In this example, a 25/75 SBR containing 0.25 weight percent of 2-(N-hexamethyleneimino)-methyl 1,3-butadiene

30   was prepared using the procedures described in Example 6 except that 1.2 grams of 2-(N-hexamethyleneimino)-methyl 1,3-butadiene was added to the polymerization mixture at the end of polymerization (90 minutes). The polymerization

was continued for another 30 minutes at 70°C. The
characterization data of this polymer are listed in Table
2.

5

TABLE 2

Example No.	wt % HMI-Monomer	Mode of HMI-Monomer addition	Tg (°C)	ML-4	Mn	Mw	Mw/Mn
7	0.25	initial charge	-36	21	126,000	128,000	1.01
8	0.50	initial charge	-32	27	139,000	142,000	1.03
6	1.00	initial charge	-33	27	129,000	136,000	1.05
11	0.50	pre-reacted	-33	27	133,900	136,300	1.02
12	0.10	pre-reacted	-33	26	136,600	138,800	1.02
13	0.25	pre-reacted	-37	24	129,000	136,000	1.02
14	0.50	sequential	-36	21	81,600	86,730	1.06 (50%)
					212,000	235,600	1.11 (50%)
15	0.10	sequential	-35	25	115,900	121,300	1.05 (80%)
					257,600	265,200	1.03 (20%)
16	0.25	sequential	-33	24	95,800	100,000	1.04 (57%)
					227,000	245,200	1.08 (43%)
17	0.25	end charge	-33	29	138,400	140,200	1.01

25

Comparative Example 18

In this example, a styrene-butadiene rubber containing
2% of pyrrolidine functional groups was prepared by co-
polymerizing styrene,1,3-butadiene monomers and 3-(2-N-
pyrrolidinoethyl) styrene. The procedure described in
Example 6 was employed except that 9.2 grams of a neat 3-
(1-N-pyrrolidinoethyl) styrene was used instead of 2-(N-
hexamethyleneimino)-methyl 1,3-butadiene. Based on GC
analysis of the residual monomer, the polymerization was
also completed in 90 minutes at 70°C. The GC data also
indicated that 3-(2-N-pyrrolidinothyl) styrene was randomly
distributed along the polymer chains.

The styrene-butadiene rubber (SBR) produced was
determined to have a glass transition temperature (Tg) at -
30°C. It was also determined to have a microstructure which
contained 42 percent 1,2-polybutadiene units, 32 percent

1,4-polybutadiene units, 24 percent random polystyrene units and 2% 3-(2-N-pyrrolidino-ethyl) styrene units. The Mooney viscosity (ML-4) at 100^{0}C for this SBR was determined to be 27. The GPC data of this polymer was also determined to have a Mn of 131,000 and Mw of 134,000. The polydispersity (Mw/Mn) was 1.02

Comparative Examples 19-20

In these examples, 25/75 SBR containing 2 weight percent of HMI and piperidine functional groups were prepared using the procedures described in Example 18 except that 3-(2-N-hexamethyleneiminoethyl) styrene and 3-(1-N-piperidinoethyl) styrene, were added in place of 3-(1-pyrrolidinoethyl) styrene, to the premix, respectively prior to polymerization. The Tg and Mooney ML-4 viscosity of these two amine functionalized SBRs were -30^{0}C, 26 and -31°C, 28, respectively.

Example 21

In this example, a 25/75 SBR containing 1 weight percent of di-allylamine functional groups was prepared using the procedures described in Example 18 except that 3-(1-N-diallylaminoethyl) styrene was used instead of 1-(2-N-pyrrolidinoethyl) styrene. The polymer was determined to have a Tg at -40°C.

Example 22

In this experiment, a high trans 10/90 SBR containing 0.5% pyrrolidine functional groups was prepared. 2150 g of a silica/alumina/molecular sieve dried premix containing 19.50 weight percent styrene/1,3-butadiene in hexane was charged into a one-gallon (3.8 liters) reactor. 2.1 grams of 2-(N-hexamethylene-imino)-methyl 1,3-butadiene was also

added to the reactor. 20 ml of a 0.172 M pre-alkylated
barium catalyst (prepared by reacting one mole of barium
salt of di(ethylene glycol)ethylether (BaDEGEE) in
ethylbenzene with 4 moles tri-n-octylaluminum (TOA) in
hexanes at 70°C)and 7 ml of 1.6 M solution of n-
butyllithium (n-BuLi) in hexanes were added to the reactor
The polymerization was carried out at 100°C for 3 hours.
The GC analysis of the residual monomer contained in the
polymerization mixture indicated that the total monomer
conversions 96% and disappearance of 2-(N-hexamethylene-
imino)-methyl 1,3-butadiene monomer. One ml of neat ethanol
was added to shortstop the polymerization. The polymer
cement was then removed from the reactor and stabilized
with 1 phm of antioxidant. After evaporating hexanes, the
resulting polymer was dried in a vacuum oven at 50°C.

The HTSBR produced was determined to have a glass
transition temperature (Tg) at -83°C and a melting
temperature, Tm at 17°C. It was then determined to have a
microstructure which contained 3.5 percent 1,2-
polybutadiene units, 14.4 percent cis-1,4-polybutadiene
units 74.5% trans-1,4-polybutadiene units and 7.6%
polystyrene. Both NMR and GPEC indicated the presence of
HMI functional groups.

The Mooney viscosity (ML-4) at 100 °C for this polymer
was determined to be 98. The GPC measurements indicated
that the polymer has a number average molecular weight (Mn)
of 107,5000 and a weight average molecular weight (Mw) of
187,30,000. The polydispersity (Mw/Mn) of the resulting
polymer is 1.74.

Examples 23-24

In these examples, high trans polybutadiene and SBR
containing 1.0 weight percent of pyrrolidine functional

groups were prepared by using 3-(2-N-pyrrolidinoethyl)styrene as a comonomer. The procedures described in Example 22 were used in these examples except that 1,3-butadiene was used as the main monomer in Example

5   23. In the procedure used, 3-(2-N-pyrrolidinoethyl)styrene was used instead of 2-(N-hexamethylene-imino)-methyl 1,3-butadiene. The polymerization was conducted at 70°C for 4 hours. The polymer characterization data of these polymers are listed in Table 3.

10

Table 3

Example No	Polymer	% pyrrolidine	Tg (^{0}C)	Tm (^{0}C)	GPC Mn	Mw	Mw/Mn
23	HTPBD	1.0	-90	35, 45, 59	83,400	100,500	1.21
24	HTSBR	1.0	-84	27, 39	69,540	81,300	1.17

20

Example 25

In this example, a cis-1,4- polybutadiene containing 0.5 weight percent of 2-(N-hexamethyleneimino)-methyl 1,3-butadiene was prepared in a bottle using a catalyst

25   consisting of neodymium neodecanoate/ tri-n-octylaluminum/t-butylchloride, at a 1/10/2 molar ratio, at 70 ^{0}C for 1 hours. GC analysis of residual monomer showed the polymerization was completed. 2-(N-hexamethyleneimino)-methyl 1,3-butadiene also was consumed. The polybutadiene

30   produced was determined to have a glass transition temperature (Tg) at - 111 ^{0}C and a melting peak at -6^{0}C. It was also determined to have a microstructure which contained 0.7 percent 1,2-polybutadiene units, 99.3 percent 1,4-polybutadiene units. The polymer was also determined to

35   have a Mn of 324,000 and a Mw of 815,000. The polydispersity (Mw/Mn) was 2.51. The presence of HMI functional groups was also verified by GPEC method.

Example 26

In this example, a cis-1,4- polyisoprene containing 0.5 weight percent of 2-(N-hexamethyleneimino)-methyl 1,3-butadiene was prepared in a bottle using a catalyst consisting of neodymium neodecanoate/ tri-n-octylaluminum/t-butylchloride, at a 1/10/2 molar ratio, at 70°C for 2 hours. GC analysis of residual monomer showed the polymerization was completed. 2-(N-hexamethyleneimino)-methyl 1,3-butadiene also was consumed. The polyisoprene produced was determined to have a glass transition temperature (Tg) at -67°C. The polymer was also determined to have a Mn of 497,000 and a Mw of 1,207,000. The polydispersity (Mw/Mn) was 2.42. The presence of HMI functional groups was also verified by NMR and GPEC techniques.

Comparative Example 27

One mole of neat piperidine was added under nitrogen to a round bottom flask containing 500 ml of 20-35% aqueous sodium hydroxide. The round bottom flask was equipped with a mechanical stirrer. The mixture was then cooled to 40°F and one mole of 4-vinyl benzyl chloride or a mixture of 3-vinyl benzyl chloride and 4-vinyl benzyl chloride was added drop-by-drop to the mixture for a period of 30-60 minutes at a temperature of 40°F to 50°F. Upon completion of the addition, the reaction mixture was heated to room temperature with the stirring being continued for a period of 2 to 4 hours. The reaction mixture was then extracted with toluene or diethyl ether. The organic filtrate was then dried over potassium hydroxide (KOH) pellets.

The toluene or diethyl ether was then removed from the dried filtrate using a rotary evaporator under reduced

pressure. The neat pyrrolidinomethyl styrene was then recovered by vacuum distillation. The boiling points of the mixture of 3-N-piperidinomethyl styrene and 4-N-piperidinomethyl styrene was 115-120°C at 0.5 mm-Hg. The yield was about 70 percent.

By utilizing a similar procedure 4-N-hexamethylene iminomethyl styrene, 4-N-pyrrolidino methyl styrene, and 4-N-dialkyl amino styrene or mixtures of 3-isomers and 4-isomers can be prepared.

Comparative Examples 28-32

In this series of experiments the rubber samples made in Examples 6-10 were compounded with 55 phr (parts by weight per 100 parts by weight of rubber) of carbon black and cured. The physical properties of the compounded rubber samples are shown Table 4.

Table 4

Example	Rubber from Example No.	Percent Functionalized Monomer	Uncured G' (15% @ 0.83 Hz)	Cured G' (5% @ 1Hz)	Cured tan delta (5% @ 1 Hz)
28	10	0.0	142 kPa	2.0 MPa	0.178
29	7	0.25	192 kPa	1.6 MPa	0.113
30	8	0.50	242 kPa	1.8 MPa	0.122
31	6	1.0	281 kPa	1.5 MPa	0.119
32	9	0.5*	405 kPa	1.6 MPa	0.097

*   The rubber was also coupled with tin tetrachloride $(SnCl_4)$.

This series of experiments shows that the solution elastomer compositions with functionalized monomers exhibited increased uncured viscosity (G' at 15% strain) indicating the presence of strong interactions between

polymer and filler. The composition with functional comonomer also showed significantly reduced tan delta values indicating that improved rolling resistance would be realized if the rubber was used in tire tread compounds.

Example 33

In this experiment 3-(2-Pyrrolidinoethyl) and 4-(2-Pyrrolidinoethyl) styrene were syntnesized. In the procedure used 1030 g of 80% Divinylbenzene (824 g of pure divinylbezene 6.324 moles; the ratio of meta-DVB to para-DVB was normally 60:40) was added under nitrogen to a 5 litter flask equipped with a stirrer that contained 2 liters of dry hexane (the use of solvent is optional, however the temperature is typically maintained at about −20°C. To this homogenous solution was added 6.239 moles (450 g or 528 ml of dry prrolidine). This homogenous solution was cooled with a mixture of ice and acetone to negative 10°C. At this temperature, 2.5% of the 6329 mmoles which is 155.9 mmoles of n-Butyllithium was added all at once. The reaction temperatures rose to +55°C. The reaction was allowed to cool to 5°C for one hour. After that the reaction was neutralized with distilled water, three samples were taken for GC analysis. Sample 1 is taken when all the ingredients are added except the catalyst, n-Butyllithium. Sample 2 was taken after the n-Butyllithium is added. Sample 3 was taken after the water was added. The GC analysis is below, Figures 1-3.

Gas Chromatography (GC) was used to monitor the
conversion of the divinylbenzene (DVB) and pyrrolidine into
the 1-pyrrolidino ethyl styrene (PES) monomer. Figure 1
5   (Sample 1) shows the initial charge of DVB and pyrrolidine
in the reactor. In Figure 1, the elution times and
relative amounts of materials are shown. For example,
hexane has an elution time of 5.7 minutes and a normalized
amount of 56.32%. Ethylbenzene and DVB are as follows:
10   11.36 and 11.44 minutes are both ethylbenzene peaks,
whereas at 11.61 and 11.72 minutes the meta- and para- DVB
peaks are seen. From the data, 34.6% of the mixture
appears to be DVB.

```
AREA%
        RT        AREA  TYPE  WIDTH       AREA%
     4.595         339   BP    .007      .00932
     4.701        1084   PB    .022      .02981
     5.700     2048127   ++    .029    56.32285
    11.360      164258   BV    .041     4.51704
    11.439      136359   UB    .040     3.74983
    11.612      861395   PV    .049    23.68809
    11.715      380831   UB    .043    10.47273
    12.192        2161   PB    .062      .05943
    16.025       41852   BB    .190     1.15092

TOTAL AREA=3636406
MUL FACTOR=1.0000E+00
```

15   Figure 1. Gas Chromatograph of initial charge
        of DVB and pyrrolidine into the reactor (Sample 1)

Figure 2 (Sample 2) monitors the reaction conversion
just after the addition of n-butyllithium (n-BuLi). In
20   this chromatograph, the elution times are very similar to
those in Figure 1: 5.7 minutes - hexane, 11.36 and 11.44
minutes - ethylbenzene, 11.60 and 11.69 minutes - meta- and

para- DVB, and the meta- and para- PES (product) is eluded at 17.35 and 17.79 minutes. As shown here, the reaction is quite fast. The amount of DVB left is roughly 9.26%, which means 73% conversion based upon the DVB.

5

```
AREA%
       RT        AREA  TYPE  WIDTH        AREA%
    4.702         894    PB   .019       .02446
    5.700     1740519    ++   .029     47.62819
   11.360      132588    BU   .040      3.62819
   11.438      122925    UB   .040      3.36376
   11.595      282819    BU   .043      7.73916
   11.691       31833    UB   .041       .87109
   12.192        2221    PB   .064       .06078
   16.254      198043    BB   .258      5.41932
   16.610       39871    BB   .055      1.89104
   16.954       14928    PB   .057       .40850
   17.348      660404    PB   .074     18.07154
   17.790      427343    PB   .070     11.69397

TOTAL AREA=3654389
MUL FACTOR=1.0000E+00
```

Figure 2. Gas Chromatograph after the addition of n-BuLi (Sample 2)

10   Figure 3 (Sample 3) is the gas chromatograph of the reaction one hour after the addition of the n-BuLi. Once again the elution times are nearly identical to those seen in Figure 2. Here the DVB amounts to 6.87%, which corresponds to nearly 80% conversion based on DVB.

```
AREA%
    RT       AREA  TYPE   WIDTH       AREA%
   4.595       156   BP    .003      .00438
   4.702       875   PB    .018      .02455
   5.700   1802240   ++    .029    50.56275
  11.360    130641   BV    .040     3.66520
  11.438    125575   VB    .040     3.52307
  11.593    220571   BV    .042     6.18823
  11.690     18478   VB    .041      .51841
  12.192      2444   PB    .067      .06857
  14.335      9175   BB    .226      .25741
  16.611     53265   BB    .054     1.49438
  16.955     20423   BB    .057      .57298
  17.355    729062   PB    .075    20.45419
  17.796    451459   PB    .071    12.66591

TOTAL AREA=3564365
MUL FACTOR=1.0000E+00
```

Figure 3. Gas chromatograph after one hour of reaction time (Sample 3)

After drying the reaction mixture with magnesium sulfate, the hexane in the filtrate was evaporated and the resulting residue was distilled at reduced pressure to yield a mixture of 3 and 4-(2-pyrrolidinoethyl)styrene. The boiling point was 105-110°C at 0.3 mm-Hg. The product contains 96% of a mixture of 3-(2-pyrrolidinoethyl) styrene and 4-(2-pyrrolidinoethyl) styrene and 4% of a mixture of 3-(2-pyrrolidinoethyl) styrene and 4-(2-pyrrolidinoethyl)-1-ethylbenzene as determined by proton NMR in CDCl3. The ratio of 3-(2-pyrrolidinoethyl)styrene to 4-(2-pyrrolidinoethyl)styrene was normally 60:40.

Example 34

In this experiment, a 2/18/80 pyrrolidinoethylstyrene/styrene/1,3-butadiene terpolymer was prepared. In the procedure used, 2068 grams of a silica/alumina/molecular sieve dried premix containing 20.14 weight percent of

pyrrolidinoethyl styrene, styrene and 1,3-butadiene in
hexane was charged into a one-gallon (3.8 liters) reactor.
The pyrrolidinoethylstyrene (PES) used contained a mixture
of 3-(2-pyrrolidinoethyl) styrene and 4-(2-

5   pyrrolidinoethyl) styrene and a small amount of mixed 3-(2-
pyrrolidinoethyl)-1-ethylbenzene and 4-(2-
pyrrolidinoethyl)-1-ethylbenzene. The ratio of 3-(2-
pyrrolidinoethyl) styrene to 4-(2-pyrrolidinoethyl)styrene
could be varied, although it was normally 60:40. The ratio

10   of PES to styrene to 1,3-butadiene ratio was 2:18:80.
Then, 0.48 ml of neat N,N,N',N'-tetramethylethylenediamine
(TMEDA) and 1.5 ml of 1.6 M n-butyl lithium (n-BuLi) in
hexanes solvent were added to the reactor. The molar ratio
of TMEDA to n-BuLi was 1.5:1. The polymerization was

15   carried out at a temperature of 70°C for 90 minutes. A GC
analysis of the residual monomer contained in the
polymerization mixture indicated that the all monomers had
been consumed by this time. The polymer cement was then
shortstopped with ethanol and removed from the reactor and

20   stabilized with 1 phm of antioxidant. After evaporating
hexane, the resulting polymer was dried in a vacuum oven at
50°C. The GC analysis of the residual monomer with respect
to the polymerization time also indicated that PES was
randomly distributed along the polymer chain.

25   The PES-styrene-butadiene terpolymer produced was
determined to have a glass transition temperature (Tg) at
- 34°C. It was also determined to have a microstructure
which contained 48.0 percent 1,2-polybutadiene units, 32.9
percent 1,4-polybutadiene units, 17.4 percent random

30   polystyrene units and 1.7 percent of PES units. The Mooney
viscosity (ML-4) at 100°C for this polymer was determined to
be 42. The GPC data of this polymer was also determined to
have a number average molecular weight (Mn) of 181,900 and

weight average molecular weight (Mw) of 190,700. The polydispersity (Mw/Mn) of the polymer was 1.05.

Other PES-styrene-butadiene terpolymers containing 0.25, 0.5, 1.0 and 5.0 weight percent PES having similar glass transition temperatures within the range of -32°C to -37°C were prepared similarly for compound evaluation.

Comparative Example 35

In this example, a 2/18/80 pyrrolidinomethylstyrene/styrene/1,3-butadiene terpolymer was prepared using the procedures described in Example 34 except that pyrrolidinomethyl styrene (PMS) was used instead of PES. The PMS was prepared from vinylbenzylchloride and normally was a mixture 3-pyrrolidino methyl) styrene and 4-(pyrrolidino methyl) styrene. The molar ratio of 3-(pyrrolidinomethyl) styrene to 4-(pyrrolidino methyl) styrene was normally closed to 60:40. Also, 0.55 ml of a neat TMEDA and 2.1 ml of 1.6 M n-BuLi were used as the initiator.

The PMS-styrene-butadiene terpolymer produced was determined to have a glass transition temperature (Tg) at -34°C. The Mooney viscosity (ML-4) at 100^0C for this polymer was determined to be 37. The GPC data of this polymer was also determined to have a Mn of 147,100 and Mw of 180,600. The polydispersity (Mw/Mn) was 1.23. The polydispersity of this polymer is significantly higher than that of PES-styrene-butadiene terpolymer obtained in Example 1 (1,23 vs. 1.05), indicating side reactions might occur when PMS was used as a co-monomer.

Example 36

In this experiment, a tin coupled 1/19/80 pyrrolidinoethylstyrene/styrene/1,3-butadiene terpolymer

was prepared. A total of 2006 grams of a
silica/alumina/molecular sieve dried premix containing 20.4
weight percent of pyrrolidinoethyl styrene (PES), styrene
and 1,3-butadiene in hexane was charged into a one-gallon
5 (3.8 liters) reactor. The PES to styrene to 1,3-butadiene
ratio was 1:19:80. Then, 0.52 ml of neat N,N,N',N'-
tetramethylethylenediamine (TMEDA) and 2.0 ml of 1.6 M n-
butyl lithium (n-BuLi) in hexane were added to the reactor,
respectively. The polymerization was carried out at 70°C
10 for 90 minutes. The GC analysis of the residual monomer
contained in the polymerization mixture indicated that all
of the monomer had been consumed by that time. Then, 250
grams of the polymer cement was removed from the reactor
and stabilized with 1 phm of antioxidant. Then, 1.30 ml of
15 a 1 M tin tetrachloride solution in hexane was added to the
remaining cement in the reactor. The molar ratio of tin
tetrachloride to n-BuLi was 0.5:1. The coupling reaction
was conducted at 70°C for 30 minutes. The polymer cement
was then removed from the reactor and stabilized with 1 phm
20 of antioxidant. After evaporating the hexane solvent, the
resulting polymer was dried in a vacuum oven at 50°C.

The PES-styrene-butadiene terpolymer or the
pyrrolidino 1- methyl-2-ethyl)α methyl styrene (PAMS)
containing styrene-butadiene terpolymer rubber produced was
25 determined to have a glass transition temperature (Tg) at -
35°C. The Mooney viscosity (ML-4) at 100°C for this polymer
was determined to be 81. The Mooney ML-4 viscosity of the
base polymer was also determined to be 16. The GPC data
indicated that the coupling efficiency was 75%.

30

Examples 37-40

In these examples, tin coupled PES-styrene-butadiene
rubber or PAMS-styrene-3-(pyrrolidino-1-Methyl-2-ethyl)α

Methyl styrene terpolymer rubber containing 0.25%, 0.5%, 2.0% and 5.0% PES were prepared using the procedures described in Example 3 except that the amount of PES was changed from 1.0% to 0.25%, 0.5%, 2.0% and 5,0%. The molar ratio of tin tetrachloride to n-BuLi was held constant at 0.5:1. The Tg, Mooney ML-4 viscosity and the percent coupling of these polymers are listed in Table 5.

Table 5

Example	%PAMS	Tg (°C)	ML-4 Base	ML-4 Coupled	% Coupling
37	0.25	-36	25	106	80
38	0.50	-39	19	95	77
36	1.00	-35	16	81	75
39	2.00	-35	17	65	-
40	5.00	-37	16	81	-

Example 41

In this example, a silicone coupled PES-styrene-butadiene terpolymer containing 2.0% PES was prepared using the procedures described in Example 36 except that the amount of PES was changed from 1.0% to 2.0% and silicon tetrachloride was used as the coupling agent. The molar ratio of silicon tetrachloride to n-BuLi was kept the same (0.5:1). The polymer was determined to have a glass transition temperature (Tg) at -36°C. The Mooney viscosity of base and silicon coupled polymers were 17 and 86, respectively.

Examples 42-43

In these examples, coupled functionalized styrene-butadiene terpolymers containing 1.0% PES or PAMS were prepared using the procedures described in Example 36 except that the silicon tetrachloride, and a mixture

containing 50% tin tetrachloride and 50% silicon
tetrachloride were used as coupling agents. The molar
ratio of coupling agent to n-BuLi was kept the same
(0.5:1). The glass transition temperature (Tg), Mooney
viscosity, and the percent of coupling agent used are
listed in Table 6.

Table 6

Example	%PAMS	Coupling agent	Tg (^{0}C)	ML-4 Base	Coupled	% Coupling
42	1.00	SiCl4	-32	21	97	81
43	1.00	50/50 SiCl4/SnCl4	-33	21	89	75

Examples 44-45

In these examples, tin coupled PES-styrene-butadiene
terpolymers containing 1.0% PES were prepared using the
procedures described in Example 36 except that the molar
ratio of tin tetrachloride to n-BuLi was changed from 0.5:1
to 0.25:1 and 0.375:1, respectively. The Tg, Mooney
viscosity and the percent coupling of these polymers are
listed in Table 7.

Table 7

Example	%PAMS	SnCl4/n-BuLi ratio	Tg (°C)	ML-4 Base	Coupled	% Coupling
44	1.00	0.25:1	-36	13	81	81
45	1.00	0.375:1	-37	12	77	77
36	1.00	0.50:1	-35	16	81	75

Comparative Examples 46

In this example, tin coupled PAMS-styrene-butadiene
terpolymer containing 1.0% PAMS was prepared using the
procedures described in Example 36 except that the molar

ratio of tin tetrachloride to n-BuLi was changed from 0.5:1
to 0.25:1. The Tg, Mooney viscosity and the percent
coupling of this polymer are listed in Table 8. As shown
in Table 8, a PES functionalized polymer can be more

5 effectively coupled with tin tetrachloride than the PMS
functionalized polymer. Polymers with better tin coupling
normally provide better compound properties.

Table 8

Example	% Functional monomer	SnCl₄/n-BuLi ratio	Tg (^{0}C)	ML-4 Base	Coupled	% Coupling
46	1% PMS	0.25:1	-33	18	65	62
44	1% PAMS	0.25:1	-36	13	81	81

Example 47

In this example, a 1%/11%/88% PES/styrene/1,3-
butadiene terpolymer or a PAMS/styrene/1,3-butadiene

20 terpolymer was prepared using the procedure described in
Example 34 except that the ratio of PES to styrene and to
1,3-butadiene was changed to 1:11:80 and the molar ratio of
TMEDA to n-BuLi was also changed to 1:1. GC analysis of
residual monomer with respect to polymerization time

25 indicated that PES was randomly distributed along the
polymer chain. The resulting terpolymer had a Tg at -42°C
and was determined to a have a ML-4 of 47.

Example 48

30 In this example, a 1%/99% PES/isoprene copolymer or a
10%/99% PAMS isoprene copolymer was prepared using the
procedure described in Example 34 except that a mixture of
PES and isoprene in hexane was used as the monomer premix
and DTP (2,2-di- tetrahydrofuryl propane) was used as the

35 modifier. The molar ratio of DTP to n-BuLi was 2.5:1. GC

analysis of residual monomer indicated that the polymerization was completed in an hour. The resulting copolymer had a Tg at -14°C and was determined to a have a ML-4 of 82.

5

Examples 49-65

In this series of experiments tire tread compounds that were loaded with carbon black as a filler were made with styrene-butadiene rubber that had various amounts of a
10   mixture of 3-(2-pyrrolidinoethyl)styrene and 4-(2-pyrrolidinoethyl)styrene or PAMS incorporated therein. The amount of functionalized styrene monomer that was incorporated into the styrene-butadiene rubber is shown in Table 9. These tire tread compositions were made by mixing
15   55 phr (parts by weight per 100 parts by weight of rubber) of N299 carbon black, 10 phr of processing oil, 3 phr of zinc oxide, 2 phr of stearic acid, 1.5 phr of antioxidant, 1.2 phr of sulfenamide accelerator, and 1.4 phr of sulfur into various styrene-butadiene rubbers having different
20   contents of bound functionalized styrene monomer. The characterization of the tire tread compounds made are shown in Table 9 (G' was measure on uncured compounds and tan delta was measured on cured samples at 60°C).

Table 9

Example	PES	Macrostructure	ML-4*	G' (kPa)	Tan delta
49	0%	linear	41	500	0.177
50	0%	linear	63	595	0.170
51	0.25%	linear	65	584	0.149
52	0.25%	linear	66	606	0.135
53	0.5%	linear	27	499	0.165
54	0.5%	linear	27	500	0.145
55	0.5%	linear	32	520	0.146
56	0.5%	linear	60	614	0.124
57	0.5%	tin coupled	77	549	0.105
58	1%	linear	47	612	0.116
59	1%	linear	62	645	0.106
60	1%	tin coupled	68	504	0.108
61	2%	linear	25	393	0.160
62	2%	linear	36	466	0.135
63	2%	linear	65	554	0.124
64	5%	linear	46	540	0.115
65	10%	linear	44	581	0.107

* Mooney ML 1+4 viscosity

It is desirable for tan delta to be as low as possible at 60°C because the hysteresis of rubber is lower at lower tan delta values. Accordingly, tire tread compound that have lower tan delta values will have less heat build-up and lower rolling resistance. As can be seen from Table 9, the incorporation of the PES or PAMS into the styrene-butadiene rubber caused a reduction in tan delta at 60°C. The incorporation of 0.25 weight percent of PMS into the styrene-butadiene rubber caused a significant reduction in tan delta. The incorporation of higher level of bound PES into the styrene-butadiene rubber caused greater reduction

in tan delta values.

Examples 66-86

In this series of experiments tire tread compounds
were make with styrene-butadiene rubber that had various
amounts of a mixture of 3-(2-pyrrolidinoethyl)styrene and
4-(2-pyrrolidinoethyl)styrene (PES)or 3-(pyrrolidino 1-
methyl-2-ethyl)α-methyl styrene(PAMS) incorporated therein.
The amount of functionalized styrene monomer that was
incorporated into the styrene-butadiene rubber is shown in
Table 10. These tire tread compositions were made as
described in Examples 49-65. The characterization of the
tire tread compounds made are shown in Table 10 (G' was
measure on uncured compounds and tan delta was measured on
cured samples at 60°C).

Table 10

Example	PES	Macrostructure	ML-4*	G' (kPa)	Tan delta
66	0%	linear	41	500	0.177
67	0%	linear	63	594	0.170
68	0.25%	linear	25	556	0.127
69	0.25%	linear	32	597	0.114
70	0.25%	linear	49	610	0.107
71	0.25%	tin coupled	106	612	0.104
72	0.5%	linear	19	590	0.119
73	0.5%	linear	30	609	0.110
74	0.5%	linear	49	608	0.088
75	0.5%	tin coupled	95	627	0.094
76	1%	linear	16	510	0.122
77	1%	linear	42	620	0.105
78	1%	tin coupled	81	570	0.091
79	2%	linear	17	517	0.110
80	2%	linear	42	619	0.096
81	2%	linear	60	619	0.085
82	2%	tin coupled	65	572	0.091
83	5%	linear	25	605	0.091
84	5%	tin coupled	47	554	0.101
85	5%	linear	48	628	0.084
86	5%	tin coupled	64	672	0.080

* Mooney ML 1+4 viscosity

As has been explained it is desirable for the tan delta of tire tread compounds to be as low as possible. As can be seen from Table 10, the incorporation of the PES into the styrene-butadiene rubber caused a reduction in tan delta at 60°C. As can been seen by comparing Table 10 to Table 9, the incorporation of PES into the styrene-butadiene rubber caused a greater reduction in tan delta

than did the incorporation of PES into the styrene-butadiene rubber.

<div align="center">Examples 87-91</div>

5   In this series of experiments tire tread compounds that were loaded with silica as a filler were make with styrene-butadiene rubber that had various amounts of a mixture of 3-(2-pyrrolidinoethyl)styrene and 4-(2-pyrrolidinoethyl)styrene (PES) incorporated therein.   The

10   amount of functionalized styrene monomer that was incorporated into the styrene-butadiene rubber is shown in Table 11.   These tire tread compositions were made by mixing 55 phr of silica, 10 phr of processing oil, 3 phr of zinc oxide, 2 phr of stearic acid, 1.5 phr of antioxidant,

15   1.5 phr of sulfenamide accelerator, and 1.4 phr of sulfur into styrene-butadiene rubbers having different contents of bound functionalized styrene monomer.   The characterization of the tire tread compounds made are shown in Table 11 (G' was measure on uncured compounds and tan delta was measured

20   on cured samples at 60°C).

<div align="center">Table 11</div>

Example	PES	ML-4*	G' (kPa)	Tan delta
87	0%	41	890	0.235
88	1%	47	800	0.157
89	5%	46	596	0.098
90	10%	44	674	0.086
91	20%	47	441	0.088

* Mooney ML 1+4 viscosity

25   As has been explained it is desirable for the tan delta of tire tread compounds to be as low as possible. As can be seen from Table 11, the incorporation of the PMS

into the styrene-butadiene rubber caused a reduction in tan
delta at 60°C. Higher levels of PES caused greater
reductions in tan delta. This series of experiments also
that it is possible to eliminate silica coupling agent from
5   tire tread compounds that are made utilizing styrene-
butadiene rubbers that contain a small amount of bound PMS.

Examples 92-96

     In this series of experiments tire tread compounds
10   that were loaded with silica as a filler were make with
styrene-butadiene rubber that had various amounts of a
mixture of 3-(2-pyrrolidinoethyl)styrene and 4-(2-
pyrrolidinoethyl)styrene (PES) or 3-(pyrrolidinolmethyl 2-
ethyl)α-methyl styrene (PAMS) incorporated therein. The
15   amount of functionalized styrene monomer that was
incorporated into the styrene-butadiene rubber is shown in
Table 11. These tire tread compositions were made by
mixing 55 phr of silica, 10 phr of processing oil, 3 phr of
zinc oxide, 2 phr of stearic acid, 1.5 phr of antioxidant,
20   1.5 phr of sulfenamide accelerator, 1.4 phr of sulfur, and
4.4 phr of silica coupling agent into styrene-butadiene
rubbers having different contents of bound functionalized
styrene monomer. The characterization of the tire tread
compounds made are shown in Table 12 (G' was measure on
25   uncured compounds and tan delta was measured on cured
samples at 60°C).

Table 12 (* Mooney ML 1+4 viscosity)

Example	PES/PAMS	ML-4*	G' (kPa)	Tan delta
92	0%	41	754	0.173
93	1%	47	720	0.132

94	5%	46	647	0.098
95	10%	44	617	0.081
96	20%	47	474	0.087

As has been explained it is desirable for the tan delta of tire tread compounds to be as low as possible. As can be seen from Table 12, the incorporation of the PMS into the styrene-butadiene rubber caused a reduction in tan delta at 60°C. Higher levels of PMS caused greater reductions in tan delta. This series of experiments also that it is possible to reduce the level of silica coupling agent in tire tread compounds that are made utilizing styrene-butadiene rubbers that contain a small amount of bound PMS and still realize good results.

<u>Examples 97-102</u>

In this series of experiments tire tread compounds that were loaded with silica as a filler were make with styrene-butadiene rubber that had various amounts of a mixture of 3-(2-pyrrolidinoethyl)styrene and 4-(2-pyrrolidinoethyl)styrene (PES) or 3-(pyrrolidinol-methyl-2-ethyl)α-metyl styrene (PAMS) incorporated therein. The amount of functionalized styrene monomer that was incorporated into the styrene-butadiene rubber is shown in Table 13. These tire tread compositions were made by mixing 78 phr of silica, 28 phr of processing oil, 2.5 phr of zinc oxide, 2 phr of stearic acid, 3 phr of antioxidant, 3 phr of siland coupler, 1.6 phr of sulfenamide accelerator, 1.9 phr of guanadiene accelerator, and 2.1 phr of sulfur into styrene-butadiene rubbers having different contents of bound functionalized styrene monomer. The characterization of the tire tread compounds made are shown in Table 13 (G' was measure on uncured compounds and tan

delta was measured on cured samples at 60°C).

Table 13

Example	PES/PA MS	ML-4*	G' (kPa)	Tan delta
97	0%	41	465	0.145
98	0.25%	49	645	0.151
99	0.5%	49	681	0.141
100	1%	42	657	0.120
101	2%	42	749	0.102
102	5%	48	869	0.073

* Mooney ML 1+4 viscosity

5

As can be seen from Table 13, the incorporation of the PES into the styrene-butadiene rubber caused a reduction in tan delta at 60°C. Higher levels of PMS caused greater reductions in tan delta. This series of experiments also

10 that it is possible to reduce the level of silica coupling agent in tire tread compounds that are made utilizing styrene-butadiene rubbers that contain a small amount of bound PES and still realize good results.

By utilizing styrene-butadiene rubber that has been

15 modified by incorporation a small amount of PES therein tire tread compounds can be made that exhibit lower hysteresis and that can be processed more easily. Silica loaded tire tread compounds can also be made with significantly lower levels of silica coupling agent. This

20 is an extremely important benefit since silica coupling agents are expensive relative to most other materials used in tire tread compounds. The amount of silica coupling agent needed in such compounds can typically be reduced to a level within the range of 0 phs (parts by weight per 100

25 parts by weight of silica) to 5 phs. More typically the

level of silica coupling agent is reduced to be within the range of 1 phs to 4 phs. The level of silica coupling agent is most typically reduced to a level within the range of 1 phs to 2 phs.

5   Functionalized styrene monomers which are of the structural formula:

wherein n represents an integer from 4 to about 10 are some of the most beneficial functionalized styrene monomers that can be utilized in the practice of this invention. In such

20   functionalized styrene monomers it is preferred form n to represent 4 or 6. PES (wherein n represents 4) is the most preferred.

      This type of functionalized monomer (PAMS) is prepared from meta-diisopropenylbenzene using the same procedure as

25   has been described for the preparation of PES. In this manner 3-(1-methyl-pyrrolidino-2-ethyl)α-methyl styrene (PAMS) was made at 70°C. The product is isolated under vacuum 120°C at 0.15 mmHg pressure.

      While certain representative embodiments and details have been shown for the purpose of illustrating the subject

30   invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention.

Examples 103-105

In this series of experiments, a linear terpolymer containing 1% PAMS, 19% styrene, and 80% 1,3-butadiene was synthesized.

Premix Preparation

101.4 g of 93% PAMS in hexane was added to a 20.27% butadiene in hexane premix cylinder via syringe under inert atmosphere to yield a solution with a monomer weight percent ratio of 98.73% 1,3-butadiene and 1.27% PAMS. The cylinder contained 7,298.6g 1,3-Butadiene, 94.3g PAMS and 28,607.1g hexane. The cylinder contents were mixed using a high shear mixer. Note that the PAMS can be added to either butadiene or styrene in this manner. A styrene premix cylinder containing 36,000g of 20.98% styrene in hexane was then prepared.

Polymerization

The desired product was linear 1% PAMS/19% styrene/80% 1,3-butadiene copolymer with a Mooney viscosity of 75 and a Tg midpoint of -35°C made continuously. Although the desired product specifies 1% PES, this copolymer can be synthesized with a range of 0.25%-2% PAMS. To meet these desired product specifications the polymerization was performed under the following operating conditions:

- Monomer weight percent ratio into first reactor of 1% PAMS/19% styrene/80% 1,3-butadiene

- 0.6897 mmoles n-butyllithium per 100 g of monomer (Target Mn of 145,000)

- 75 parts 1,2-butadiene per million parts monomer

- 2.0 mmoles TMEDA per mole n-butyllithium

- Reactor 1 Temperature of 194°F

- Reactor 2 Temperature of 190°F

- Total retention time of 1 hour

5   The continuous unit contains two one gallon continuous stirred tank reactors (CSTR's) in series equipped with mechanical agitators under inert atmosphere, followed by a five gallon cement holding tank. Styrene, 1,3-butadiene and PAMS, 1,2-butadiene, and TMEDA were brought together

10   and then were added to the first reactor where they met the n-butyllithium. After achieving steady state, percent solids were used to monitor total monomer conversion, whereas GC analysis provided individual monomer consumption. GC results can be seen in Table 14.

15   The product was collected in a cement tank where it was terminated with 1 mole isopropanol per mole n-BuLi (shortstop) and 1 part per hundred monomer of Paratax (antioxidant). Polymer was air dried in a 130°F oven for three days. Testing of the dry raw polymer includes Mooney

20   Large, DSC, GPC and NMR. Results from these tests can be seen in Tables 15 and 16.

Table 14: Monomer Conversion via Gas Chromatograph

Total % Monomer Conversion			
% Butadiene	%Styrene	%Functional Mon.	%Total Conv.
97.95	96.36	99.88	97.67

25

Table 15: Linear Polymer Characterizations

ML+4	DSC (°C)			GPC Analysis			
	Onset Tg	Inflection Tg	End Tg	Mn	Mw	Mz	Mw/Mn
74	-42.02	-39.32	-36.67	179,500	335,500	640,200	1.87

Table 16: NMR Data for Linear Polymer

					Styrene Sequence			
Trans 1,4-BD	Cis 1,4 – BD	1,2-BD	DVCH	Styrene	1S	2-4S	>/=5S	PyrES
24.7	15.6	35.7	5.0	17.8	16.4	1.3	0.1	1.2

Coupled Polymerization of 1% PAMS/19% Styrene/80% 1,3-Butadiene

The procedures outlined above were also used for coupled polymerizations with tin tetrachloride, silicon tetrachloride, and a combination of the two. There are only slight variations in the operating conditions. The coupling agent was added at a ratio of 0.25 moles of coupling agent per mole n-butyllithium.

The desired product was coupled 1% PAMS/19% styrene/80% 1,3-butadiene copolymer with a linear base Mooney viscosity of 35, a coupled Mooney viscosity of 90 and a Tg midpoint of -35°C made continuously. To meet these specifications the polymerization was performed under the following operating conditions:

- Monomer weight percent ratio into first reactor of 1% PES/19% styrene/80% 1,3-butadiene
- 0.8091 mmoles n-butyllithium per 100 g of monomer (Target Mn of 120,000)
- 75 parts 1,2-butadiene per million parts monomer
- 2.0 mmoles TMEDA per mole n-butyllithium
- 0.25 moles 2% coupling agent (both $SnCl_4$ and $SiCl_4$) in hexane per mole n-butyllithium
- Reactor 1 Temperature of 194°F
- Reactor 2 Temperature of 190°F
- Total retention time of 1 hour

The coupling agent was introduced to the polymerization in a high shear cement mixer located after the second reactor and before the cement holding tank. The hold time in the cement mixer was approximately four minutes. Tables 17-19 include characterization data for these copolymers.

Table 17: Monomer Conversion via Gas Chromatograph

Total % Monomer Conversion			
% Butadiene	%Styrene	%Functional Mon.	%Total Conv.
99.03	98.65	99.88	98.97

Table 18: Linear Polymer Characterizations

ML+4	DSC (°C)			GPC Analysis			
Base SnCl$_4$ SiCl$_4$	Onset Tg	Inflection Tg	End Tg	Mn	Mw	Mz	Mw/Mn
42	-38.5	-35.8	-33.0	127,000	274,800	647,800	2.16
88	-40.1	-36.7	-33.3	147,900	424,100	1,471,000	2.87
74	-39.0	-36.2	-33.4	148,500	392,900	1,158,000	2.65

Table 19: NMR Data for Linear Polymer

					Styrene Sequence			
Trans 1,4- BD	Cis 1,4 - BD	1,2- BD	DVCH	Styrene	1S	2-4S	>/=5S	PyrES
21.3	15.3	37.4	5.0	20.1	18.3	1.4	0.5	0.9

Coupled Polymerization of 0.5% PAMS/19.5% styrene/80% 1,3-butadiene

Once again, the procedures outlined above were used for coupled polymerizations with tin tetrachloride, silicon tetrachloride. There are only slight variations in the operating conditions. The coupling agent was added in a ratio of 0.25 moles coupling agent per mole n-butyllithium.

The desired product was coupled 0.5% PES/19.5%

styrene/80% 1,3-butadiene SSBR copolymer with a linear base
Mooney viscosity of 27, a coupled Mooney viscosity of 90
and a Tg midpoint of -35°C made continuously. To meet these
specifications the polymerization was performed under the
following operating conditions:

- Monomer weight percent ratio into first reactor of 1%
  PES/19% styrene/80% 1,3-butadiene
- 0.8091 mmoles n-butyllithium per 100g monomer (Target
  Mn of 120,000)
- 75 parts 1,2-butadiene per million parts monomer
- 2.0 mmoles TMEDA per mole n-butyllithium
- 0.25 moles 2% coupling agent (both $SnCl_4$ and $SiCl_4$) in
  hexane per mole n-butyllithium
- Reactor 1 Temperature of 194°F
- Reactor 2 Temperature of 190°F
- Total retention time of 0.5 hours

The coupling agent is introduced to the polymerization
in a high shear cement mixer located after the second
reactor and before the cement holding tank. The hold time
in the cement mixer is approximately four minutes. Tables
20-22 include characterization data for these copolymers.

Table 20: Monomer Conversion via Gas Chromatograph

Total % Monomer Conversion			
% Butadiene	%Styrene	%Functional Mon.	%Total Conv.
98.55	96.69	99.55	98.14

Table 21: Linear Polymer Characterizations

ML+4	DSC (°C)			GPC Analysis			
Base SnCl$_4$ SiCl$_4$	Onset Tg	Inflection Tg	End Tg	Mn	Mw	Mz	Mw/Mn
32	-37.7	-35.1	-32.4	120,100	189,400	276,200	1.58
73	-38.1	-34.8	-31.5	190,100	468,500	960,800	2.46
86	-38.8	-35.6	-32.7	192,000	430,100	704,500	2.24

Table 22: NMR Data for Linear Polymer

					Styrene Sequence			
Trans 1,4- BD	Cis 1,4 - BD	1,2- BD	DVCH	Styrene	1S	2-4S	>/=5S	PyrES
22.1	15.5	37.5	4.9	19.6	17.5	1.9	0.2	0.4

Examples 106-108

High trans-SBR was synthesized in this series of experiments. In the procedure utilized polymerization of styrene, 3-pyrrolidino-ethyl-α-methyl styrene (PAMS) and butadiene was carried out in a one-gallon glass bowl batch reactor, under a blanket of nitrogen, equipped with a mechanical stirrer and temperature control via cooling water and low pressure steam. Both butadiene and styrene premixes contained approximately 20% monomer dissolved in hexane. The reactor was charged with 1% PES, 9% styrene in hexane and 90% butadiene in hexane to synthesize the appropriate polymer. The catalyst was added at room temperature, and within minutes of addition, the reactor temperature was 90°C. The catalyst system for this polymer consisted of an alkylated Barium diethyleneglycol ethylether (BaDEGEE) and Trioctyl aluminum (TOA) in a 1 (BaDEGEE) to 4 (TOA) ratio and n-butylithium. The addition of this catalyst is crictical for a successful polymerization. The alkylated BaDEGEE and TOA solution was prepared by added the appropriate amount of TOA to BaDEGEE

and heated for 30 minutes at 70°C. Pyrrolidine and TMEDA
can also be used as a modifier in this catalyst in a ratio
of 1/1 amine/BaDEGEE, and they are typically added in this
alkylation step. Here, 0.80 mmol of BaDEGEE per 100 grams
5   of polymer was used to intiate polymerization. The
alkylated BaDEGEE/TOA solution (with or without amine
present) was added to a clean bottle and the correct amount
of n-BuLi (in a ratio of 3 n-BuLi to 1 BaDEGEE) was added.
The final solution had a ratio of 1/4/3/1 BaDEGEE/TOA/n-
10 BuLi/amine (if used). This solution was shaken for several
minutes at room temperature, and then it was injected as
the initiator. Samples were taken over the course of the
reaction to determine monomer conversion. According to gas
chromatography, the PES monomer appeared to react much
15 faster than the butadiene or styrene, see Figure 1. All
reactions were short-stopped with denatured ethanol, and
2,6-ditertbutylphenol was added to the polymer cement. The
polymer was then dried for several days in a hot oven to
make sure all solvent had evaporated. Table 1 summarizes
20 the data for this system:

High trans isoprene-butadiene (IBR) was synthesized in
this experiment using the same procedure and catalyst
system as described above, by polymerization of PAMS,
isoprene and 1,3-butadiene. The only difference was that
25 the reactor was charged with 1% PES, 9% isoprene and 90%
1,3-butadiene. All other conditions were identical.
Figure 2 illustrates monomer conversion versus time.
Polymer characteristics are shown in Table 1.

High trans styrene-isoprene-butadiene rubber (SIBR)
30 was also synthesized in this experiment using the same
procedure and catalyst system outlined above by
polymerization of PAMS, styrene, isoprene and butadiene.
The only difference was that the reactor was charged with

1% PAMS, 9% isoprene 2.5% styrene *and 87.5% 1,3-butadiene.*
All other conditions were identical.

Table 23: Polymer characteristics for PAMS
containing high trans polymers

Sample	Tg (onset)	Tg (midpt.)	Tm	Mn	Mw	PDI	ML+4
1/9/90 HTPAMSSB R	-83.4°C	-76.0°C	24.2°C	135K	191K	1.42	57
10/90 HTSBR	-86.0°C	-79.7°C	17.6°C	102K	164K	1.61	66

Table 24: NMR Results for PyrAMS High Trans polymers

Sample	Trans 1,4-BD	Cis 1,4-BD	1,2-BD	Styrene	PyrAMS
1/9/90 HTPESSBR	76.0	13.2	3.4	6.5	0.9
10/90 HTSBR	75.2	13.8	3.5	7.5	—

Example 109

In this experiment, a 5/95 3-(2-pyrrolidino-1-methylethyl) -1-alpha-methyl styrene (Pyr-AMS)/1,3-butadiene co-polymer was prepared. In the procedure, 1,212 g of a silica/alumina/molecular sieve dried premix containing 20.08 weight percent of Pyr-AMS and 1,3-butadiene in hexane was charged into a one-gallon (3.8 liters) reactor. The Pyr-AMS to 1,3-butadiene ratio was 5:95. 2.6 ml of 1.0 M N, N, N', N'-tetramethylethylenediamine (TMEDA) solution in hexane, 0.81 ml of 0.4 M potassium 3,7-dimethyl-3-octanoxide in hexane and 1.3 ml of 1.0 M n-butyl lithium (n-BuLi) in hexane were added to the reactor, respectively. The molar ratio of

potassium 3,7-dimethyl-3-octanoxide to TMEDA to n-BuLi was 0.25:2:1. The polymerization was carried out at 70°C for 60 minutes. The gas chromotograph (GC) analysis of the residual monomer contained in the polymerization mixture taken periodically indicated that the polymerization rates for both Pyr-AMS and 1,3-Bd were almost identical and all monomers were consumed after about 60 minutes. This illustrates that Pyr-AMS was randomly distributed along the polymer chains. The polymerization was then shortstopped by adding ethanol to the polymer cement and then the polymer cement was removed from the reactor and stabilized with 1 phm of antioxidant. After evaporating the hexane, the resulting polymer was dried in a vacuum oven at 50°C. The Pyr-AMS-butadiene copolymer produced was determined to have a glass transition temperature (Tg) at -59°C. It was also determined to have a microstructure which contained 49.1 percent 1,2-polybutadiene units, 46.0 percent 1,4-polybutadiene units and 4.9 percent of random Pyr-AMS units. The Mooney viscosity (ML-4) at 100°C for this polymer was determined to be 59.

Example 110

In this experiment, a high trans 5/95 Pyr-AMS/butadiene copolymer was prepared. In the procedure, 1,010 g of a silica/alumina/molecular sieve dried premix containing 20.4 weight percent Pyr-IPB and 1,3-butadiene was charged into a one-gallon (3.8 liters) reactor. The Pyr-AMS to 1,3-butadiene ratio was 5:95. Then, 1.3 ml of a 0.99 M solution of a barium salt of di(ethylene glycol) ethylether (BaDEGEE) in ethylbenzene, 5.2 ml of a 1.0 M solution of tri-n-octylaluminum (TOA) in hexanes, and 2.4 ml of 1.6 M solution of n-butyllithium (n-BuLi) in hexanes were added to the reactor. The molar ratio of BaDEGEE to

TOA and to n-BuLi was 1:4:3.

The polymerization was carried out at 90°C for 4 hours. The GC analysis of the residual monomer contained in the polymerization mixture indicated that the Pyr-AMS monomer
5 was randomly distributed along the polymer chain. Then, one ml of neat ethanol was added to shortstop the polymerization. The polymer cement was then removed from the reactor and stabilized with 1 phm of antioxidant. After evaporating hexanes, the resulting polymer was dried
10 in a vacuum oven at 50°C.

The copolymer produced was determined to have a glass transition temperature (Tg) at -84°C and a melting temperature (Tm) of 9.4°C. It was then determined to have a microstructure which contained 6.2 percent 1,2-
15 polybutadiene units, 19.8 percent cis-1,4-polybutadiene units, 69.0% trans-1,4-polybutadiene units, and 5.0 percent random Pyr-AMS units. The GPC measurements indicated that the polymer had a number average molecular weight (Mn) of 96,870 and a weight average molecular weight (Mw) of
20 115,100. The polydispersity (Mw/Mn) of the resulting polymer was 1.19.

Example 111

In this experiment, a 0.5/19.5/80 Pyr-AMS/styrene/1,3-
25 butadiene terpolymer was prepared. The procedure described in Example 1 was used except that a premix containing Pyr-AMS, styrene and 1,3-butadiene in hexane at a weight ratio of 0.5:19.5:80 was used as the monomer premix solution and the molar ratio of potassium 3,7-dimethyl-3-octanoxide to
30 TMEDA to n-BuLi was 0.015:2:1. The GC analysis of residual monomer again showed that polymerization rates of the three monomers were almost identical indicating that both Pyr-AMS and styrene were randomly distributed along the polymer

chain.

The terpolymer produced was determined to have a glass transition temperature at -34°C. The Mooney viscosity (ML-4) at 100°C for this polymer was determined to be 57. The GPC measurements indicated that the polymer had a number average molecular weight (Mn) of 187,300 and a weight average molecular weight (Mw) of 191,900. The polydispersity (Mw/Mn) of the resulting polymer was 1.024.

Examples 113-115

In this series of experiments, terpolymers containing Pyr-AMS/styrene/1,3-butadiene at ratios of 2:18:80 and 5:15:80 were prepared. Procedure described in Example 3 was employed here except that the Pyr-AMS/styrene/1,3-butadiene ratios were changed from 0.5:19.5:80 to 2:18:80 and 5:15:80, respectively.

The Tg, ML-4 and GPC data of these terpolymers are listed in Table 25.

Table 25

Example	%Pyr-AMS	Tg(°C)	ML-4	Mn	Mw	Mw/Mn
113	0.5	-34	57	187,300	191,900	1.024
114	2.0	-33	59	179,000	187,200	1.046
115	5.0	-35	59	191,600	195,300	1.019

Examples 116-118

In these experiments, terpolymers containing HMI-AMS/styrene/1,3-butadiene ratios of 0.5:19.5:80, 2:18:80 and 5:15:80 were prepared. Procedures described in Examples 3, 4 and 5 were employed here except that 3-(2-hexamethyleneimino-1-methyl ethyl)-1-alpha-methyl styrene (HMI-AMS) was used instead of Pyr-AMS. The Tg, ML-4 and GPC data of these terpolymers are listed in Table 26.

Table 26

Example	%HMI-AMS	Tg (^{0}C)	ML-4	Mn	Mw	Mw/Mn
116	0.5	-35	33	142,700	148,500	1.040
117	2.0	-35	33	140,200	148,800	1.061
118	5.0	-33	44	148,200	166,400	1.123

Examples 119-121

In these experiments, terpolymers containing Pip-AMS/styrene/1,3-butadiene at ratios of 0.5:19.5:80, 2:18:80 and 5:15:80 were prepared. Procedures described in Examples 113, 114 and 115 were employed here except that 3-(2-piperidino-1-methyl ethyl)-1-alpha-methyl styrene (Pip-AMS) was used instead of Pyr-AMS. The Tg, Mooney ML-4 viscosity and GPC data for these terpolymers are listed in Table 27.

Table 27

Example	%HMI-AMS	Tg (^{0}C)	ML-4	Mn	Mw	Mw/Mn
119	0.5	-33	34	153,200	156,200	1.019
120	2.0	-35	35	140,200	155,900	1.043
121	5.0	-36	63	178,800	212,500	1.123

Example 122

In this example, an attempt was made to prepare a 5:15:80 Pyr-AMS/styrene/1,3-butadiene terpolymer without using any potassium alkoxide. The procedure described in Example 115 was used except that potassium 3,7-dimethyl-3-octanoxide was not used in the experiment. GC analysis of residual monomers showed very little Pyr-AMS was incorporated into the polymer chain until most of styrene and 1,3-butadiene monomer were consumed indicating blocky poly(Pyr-AMS) was formed at the end of polymer chains. At the end of 2 hours polymerization time, only 26% of Pyr-AMS was consumed.

The terpolymer produced was determined to have a glass transition temperature at -35°C. The Mooney viscosity (ML-4) at 100°C for this polymer was determined to be 40. The GPC measurements indicated that the polymer has a number average molecular weight (Mn) of 174,500 and a weight average molecular weight (Mw) of 177,100. The polydispersity (Mw/Mn) of the resulting polymer is 1.010.

Example 123

In this experiment, Pyrrolidine-alpha-methyl styrene (Pyr-AMS) functional monomer was incorporated into a styrene-butadiene rubber. In the procedure used, a monomer premix was made by adding 44.2 grams of 100% Pyr-AMS was added to 36,000 grams of a 19.64% 1,3-butadiene (in hexane) premix cylinder via syringe under inert atmosphere. The prepared cylinder contained 7,070.4 g 1,3-butadiene, 44.2 g Pyr-AMS and 28,929.6 g hexane. This resulted in a monomer weight percent ratio of 99.38% 1,3-butadiene and 0.62% Pyr-AMS. The cylinder contents were mixed using a high shear mixer. It should be noted that the Pyr-AMS can be added to either 1,3-butadiene or styrene in this manner. A styrene premix cylinder containing 36,000 g of 20.27% styrene in hexane was also prepared.

The desired product was a linear 0.5% Pyr-AMS/19.5% styrene/80% butadiene SSBR copolymer coupled with silica tetrachloride. The target linear base Mooney viscosity was 28-32, the target coupled Mooney viscosity was 80-100 and the target Tg midpoint was -33°C. Although the desired product in this example specifies 0.5% Pyr-AMS, this ° copolymer can be synthesized with a range of 0.25%-2% Pyr-AMS. Polymerization was performed under the following operating conditions to meet the desired product

specifications:

- Monomer weight percent ratio into first reactor of
  0.5% Pyr-AMS/19.5% styrene/80% butadiene .

5
- 0.100 mmoles n-butyllithium per 100 g monomer
  (Target Mn of 100,000)

- 80 parts 1,2-butadiene per million parts monomer

- 2.0 mmoles TMEDA per mole n-butyllithium

- 0.01 moles KOR per mole n-butylithium (can range
10   from 0.005 to 0.02 moles KOR per mole n-butylithium)

- 0.25 moles SiCl$_4$ per mole n-butylithium was added to
  the second reactor

- Reactor 1 Temperature 180°F (polymerization)

- Reactor 2 Temperature 175°F (coupling with SiCl$_4$)

15
- Total residence time of 90 minutes

The continuous unit contained two five liter CSTR's in
series equipped with mechanical agitators under an inert
atmosphere, followed by a five gallon cement holding tank.
20 Styrene, 1,3-butadiene, Pyr-AMS, 1,2-butadiene, KOR, and
TMEDA were brought together and then were added to the
first reactor where they came in contact with the n-
butyllithium. Silica tetrachloride was added to the second
reactor as a coupling agent. After achieving steady state,
25 percent solids were used to monitor total monomer
conversion, and GC analysis provided individual monomer
consumption. GC results can be seen in Table 28.
The linear product was collected from the first
reactor into a quart bottle containing 1 cc of 10%
30 isopropylalcohol (terminator) and 12 cc 10% an antioxidant.
The coupled product was collected in a cement tank where 1
part per hundred monomer of additional antioxidant was
added. Polymer was air dried in a 130°F oven for three

days. Testing of the dry raw polymer included Mooney
viscosity, DSC, GPC and NMR. Results from these tests can
be seen in Table 29.

5   Table 28: Total Monomer Conversion in Linear and Si
                    Coupled Polymerization via GC

| Polymer | Total % Monomer Conversion | | | |
	% Butadiene	% Styrene	% Funct. PyrAMS	% Total Conv.
Linear	96.51	96.64	99.72	96.55
Si Coupled	96.51	96.64	99.72	96.55

10   Table 29: Linear and Si Coupled Polymer
                         Characterizations

| Polymer | M/L-4 | Onset Tg | DSC Inflection Tg | End Tg | GPC Analysis | | | |
					Mn	Mw	Mz	Mw/Mn
Linear	21	-33.32	-29.99	-26.68	92,200	183,800	360,800	1.99
Si Coupled	96	-32.54	-29.40	-26.30	213,700	531,500	1,367,000	2.49

15   Examples 124-127

      In this series of experiments tire tread compounds
that were loaded with carbon black as a filler were made
20   with styrene-butadiene rubber that had varied amounts of
Pyr-AMS (PAMS) incorporated therein. The amount of
functionalized styrene monomer that was incorporated into
the styrene-butadiene rubber is shown in Table 30. These
tire tread compositions were made by mixing 55 phr (parts
25   by weight per 100 parts by weight of rubber) of N299 carbon
black, 10 phr of processing oil, 3 phr of zinc oxide, 2 phr
of stearic acid, 1.5 phr of antioxidant, 1.2 phr of
sulfenamide accelerator, and 1.4 phr of sulfur into various
styrene rubbers having different contents of bound
30   functionalized styrene monomer. The characterization of
the tire tread compounds made are shown in Table 30 (G' was

measured on uncured compounds and tan delta was measured on cured samples at 60°C).

Table 30

Example	% PAMS	ML-4*	G' (kPa)	Tan delta
124	0	63	595	0.170
125	0.5	57	639	0.111
126	2	59	626	0.104
127	5	59	627	0.102

* Mooney ML 1+4 viscosity

It is desirable for tan delta to be as low as possible at 60°C because the hysteresis of rubber is lower at lower tan delta values. Accordingly, tire tread compound that have lower tan delta values will have less heat build-up and lower rolling resistance. As can be seen from Table 30, the incorporation of PAMS into the styrene-butadiene rubber caused a reduction in tan delta at 60°C. The incorporation of 0.5 weight percent of PAMS into the styrene-butadiene rubber caused a significant reduction in tan delta. The incorporation of higher level of bound PAMS into the styrene-butadiene rubber caused greater reduction in tan delta values.